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JOHN MUIR INSTITUTE OF THE ENVIRONMENT

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QUALITY ASSURANCE PROJECT PLAN

(QAPP)

Sacramento, Delta and San Joaquin River Basins Organophosphorus Pesticides TMDL Monitoring Quality Assurance Project Plan

(Revision 1.0)

Prepared By

Henry Calanchini

15 February, 2005

GROUP A: PROJECT MANAGEMENT

1. APPROVAL SIGNATURES

Aquatic Ecosystems Analysis Laboratory, John Muir Institute of the Environment, University of California, Davis

Title:	Name:	Signature:	Date:
Project Manager	Michael Johnson		
QA Officer	Melissa Turner		
Project Supervisor	Henry Calanchini		

California Department of Food and Agriculture Laboratory, Sacramento

Title:	Name:	Signature:	Date:
CDFA QA Officer	Stephen Siegel		
CDFA Lab Manager	Dr. Mark Lee		

Central Valley Regional Water Quality Control Board

Title:	Name:	Signature:	Date:
Project Manager/QA Officer	Danny McClure		

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3. DISTRIBUTION LIST

Title:	Name (Affiliation):	Tel. No.:	QAPP No*:
Contractor Project Manager	Michael Johnson	(530) 752-8837	
Contractor Project Supervisor	Henry Calanchini	(530) 297-4684	
Contractor QA Officer	Melissa Turner	(530) 297-4684	
Regional Board Contract Manager	Jay Rowan (CVRWQCB)	(916) 464-4718	
Regional Board QA Officer	Daniel McClure (CVRWQCB)[1]	(916) 464-4751	
Chief, San Joaquin River TMDL Unit	Les Grober (CVRWQCB)	(916) 464-4851	
Regional Board Project Manager	Diane Beaulaurier (CVRWQCB)	(916) 464-4637	
Chief, Sacramento River TMDL Unit	Joe Karkoski (CVRWQCB)	(916) 464-4668	
Regional Board Technical Reviewer	Daniel McClure (CVRWQCB)	(916) 464-4751	
Regional Board Technical Reviewer	Zhimin Lu (CVRWQCB)	(916) 464-4830	
CDFA QA Officer	Stephen Siegel	(916) 262-1434	
CDFA Lab Manager	Dr. Mark Lee	(916) 262-1434	

[1] The CVRWQCB does not currently have a QA officer. Danny McClure will serve as acting QA manager for this project

4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

The Central Valley Regional Water Quality Control Board (CVRWQCB) is a California state regional board tasked with protecting the quality of the waters within the Central Valley Region for all beneficial uses. The CVRWQCB formulates and adopts water quality control plans for specific ground and surface water basins and prescribes and enforces requirements on waste discharges. As the contracting agency, CVRWQCB will direct UC Davis staff in sample collection techniques, sampling site locations, sampling frequency and duration and the initiation and maintenance of a contract with the California Department of Food and Agriculture's Center for Analytical Chemistry.

The Aquatic Ecosystems Analysis Lab (AEAL) of the John Muir Institute of Ecology at UC Davis, is responsible for the collection of water samples and their delivery to the California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA) Laboratory and UC Davis' in-house ELISA laboratory. AEAL will create and populate a database of project results, calculate loads of pesticides and maintain copies of field sheets and chain of custody forms. AEAL will maintain contact with the Regional Board, CDFA, and UC Davis' ELISA lab to notify of intent to sample and provide the CVRWQCB with updates on sampling progress. At the completion of monitoring, AEAL will prepare a final report to the CVRWQCB (see Table 2 for timeline).

The CDFA will be the contract laboratory for all analyses not conducted at UC Davis' in-house laboratory. CDFA will analyze submitted samples in accordance with all method and quality assurance requirements found in this QAPP. CDFA will act as a technical resource to UC Davis staff and management.

Table 1. (Element 4) Personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
Jay Rowan	CVRWQCB	Contract Manager	Ph: (916) 464-4718 Fax: (916) 464-4800 e-mail: jayrowan@waterboards.ca.gov
Melissa Turner	University of California, Davis	Contractor QA Officer	Ph: (530) 297-4684 Fax: (530) 297-4684 e-mail: mmturner@ucdavis.edu
Dr. Michael Johnson	University of California, Davis	Contractor Project Manager	Ph: (530) 752-8837 Fax: (530) 297-4684 e-mail: mbjohnson@ucdavis.edu
Henry Calanchini	University of California, Davis	Contractor Project Supervisor	Ph: (530) 297-4684 Fax: (530) 297-4684 e-mail: hjcalanchini@ucdavis.edu

Stephen Siegel	California Department of Food and Agriculture Center for Analytical Chemistry	CDFA QA Officer	Ph: (916) 262-1434 Fax: (916) 262-1572 e-mail: ssiegel@cdfa.ca.gov
Diane Beaulaurier	CVRWQCB	Regional Board Technical Reviewer	Ph: (916) 464-4637 Fax: (916) 464-4800 e-mail: dbeaulaurier@waterboards.ca.gov
Daniel McClure	CVRWQCB	Regional Board Project Manager / Project QA	Ph: (916) 464-4751 Fax: (916) 464-4780 e-mail: dmcclure@waterboards.ca.gov
Zhimin Lu	CVRWQCB	Regional Board Technical Reviewer	Ph: (916) 464-4830 Fax: (916) 464-4779 e-mail: zlu@waterboards.ca.gov

4.2 Personnel Responsibilities

Contract Manager role:
Jay Rowan is the Contract Manager. Jay Rowan is responsible for obtaining all services and analytical results/reports from the CDFA Lab Manager and all services and reports generated by the AEAL.

AEAL Quality Assurance Officer role:
Melissa Turner is the AEAL Quality Assurance Officer. Melissa Turner's role is to establish the quality assurance and quality control procedures found in this QAPP as part of the sampling, field analysis, and in-house analysis procedures. Melissa Turner will also work with Stephen Siegel, the Quality Assurance Officer for CDFA Laboratory, by communicating all quality assurance and quality control issues contained in this QAPP to the CDFA Laboratory.

Contractor Project Manager role:
Michael Johnson is the UC Davis Project Manager. He will be responsible for all aspects of the project including the organization of field staff, scheduling of sampling days, management of UC Davis' in-house ELISA laboratory, and interactions with the CDFA laboratory and the CVRWQCB.

Contractor Project Supervisor role:
Henry Calanchini is the Project Supervisor. The project supervisor will assist the project manager by hiring, training and supervising all monitoring staff and contributing to the monitoring program report. The project supervisor will be responsible for monitoring spray application and weather conditions and, in coordination with the technical reviewer, will determine when to begin sampling each storm event.

[1] The CVRWQCB does not currently have a QA officer. Danny McClure will serve as acting QA manager for this project

CDFA Quality Assurance Officer role:
Stephen Siegel is the CDFA Quality Assurance Officer. Stephen Siegel will maintain all records associated with the receipt and analysis of samples analyzed for organophosphate pesticides, and will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch.

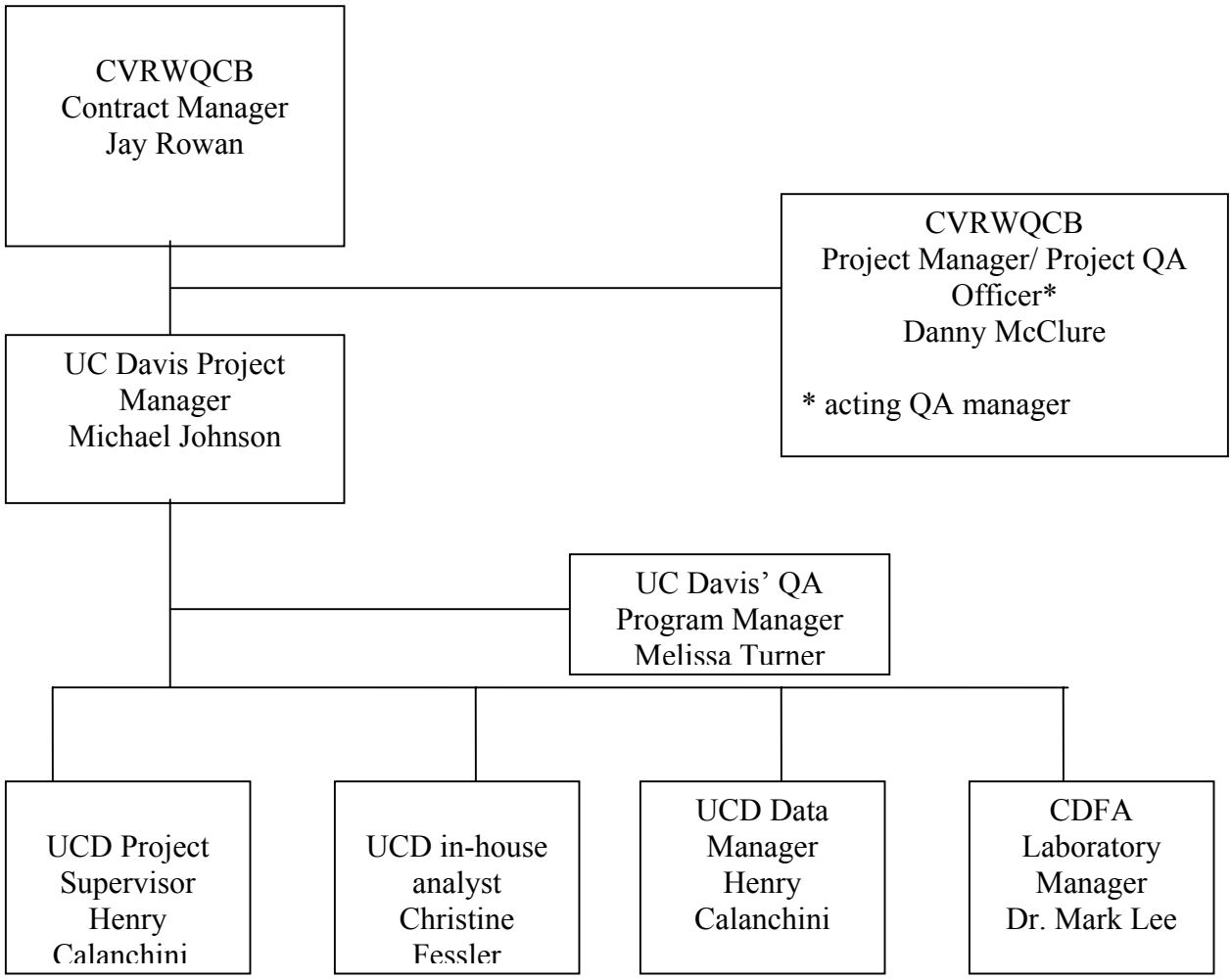
Regional Board Technical Reviewer role:
Diane Beaulaurier and Zhimin Lu are the Regional Board Technical Reviewers. The Technical Reviewers provide advice in determining the sampling sites, frequency, and time periods and are responsible for overseeing budgetary expenses related to this monitoring study.

Regional Board Project Manager/Project QA Officer role:
Danny McClure is the Regional Board Project Manager/Project Quality Assurance Officer. Danny McClure will oversee the actions of all persons maintaining records and data. He will also assist the Technical Reviewers in determining the sampling sites, frequency, and time periods and overseeing budgetary expenses related to this monitoring study. As the Project Quality Assurance Officer he will be responsible for verifying that the quality assurance and quality control procedures found in this QAPP meet the standards developed for Surface Water Ambient Monitoring Program (SWAMP) QAPPs as set forth in the Electronic Template for SWAMP-Compatible Quality Assurance Project Plans (Nichol and Reyes, 2004).
4.3 Persons responsible for QAPP update and maintenance.

Changes and updates to this QAPP may be made after a review of the evidence for change by CVRWQCB's Project Manager and Quality Assurance Officer, and with the concurrence of the Regional Board's Contract Manager. The AEAL QA Officer will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final for signature.

4.4 Organizational chart and responsibilities

Figure 1. Organizational chart.



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement.

Diazinon and chlorpyrifos are applied to orchards and field crops throughout the year to control a variety of insect pests. Pesticides are washed into mainstem rivers and tributaries by winter rains and by irrigation runoff. Pesticide concentrations in the rivers and tributaries are often toxic to aquatic invertebrates. Aquatic invertebrates are the primary source of food for larval fish. Pesticide concentrations exceed California Department of Fish and Game (CDFG) water quality criteria that are designed to protect aquatic invertebrates.

5.2 Decisions or outcomes.

This project will provide information about levels of organophosphate pesticides in water bodies of the Central Valley through the collection and analysis of water samples. This information will be used to further characterize and define the sources of diazinon, chlorpyrifos and other organophosphates that cause surface water contamination and toxic conditions to aquatic life. The results of this study will be used to support the development and implementation of Total Maximum Daily Loads (TMDL's) for diazinon and chlorpyrifos in Central Valley waterways.

5.3 Water quality or regulatory criteria

The project uses 0.080 µg/L of diazinon and 0.025 µg/L of chlorpyrifos as defining the acute, criteria maximum concentration (CMC). The CMC is a one hour average not to be exceeded more than once every three years. The criterion continuous concentration (CCC) in this project is 0.050 µg/L for diazinon and 0.014 µg/L for chlorpyrifos. The CCC is a four day average, not to be exceeded more than once every three years. These criteria were developed by the California Department of Fish and Game to protect aquatic invertebrates.

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6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

This project will monitor concentrations of diazinon, chlorpyrifos and other organophosphate pesticides, and pH, electrical conductivity and temperature at 19 waterway sites throughout the Central Valley for up to eight consecutive days during two to three winter storms. Locations for pesticide monitoring were selected on the basis of documented use of these pesticides upstream from the locations monitored, on pesticide-caused toxicity detected at these streams/rivers, and on inclusion of pesticides on the 303(d) list of impaired water bodies. Data obtained will be used to quantify ambient levels of pesticides in the Sacramento, Delta and San Joaquin River watersheds and in the development of TMDLs for tributaries within the Sacramento and San Joaquin River Basins.

6.2. Constituents to be monitored and measurement techniques.

Concentrations of diazinon, chlorpyrifos and other organophosphate pesticides will be determined with gas chromatography mass spectrometry (GC/MS). A copy of the method is attached and a demonstration of performance is available at the CDFA's Center for Analytical Chemistry. In addition, samples from the Sacramento River Basin sites will be analyzed for pesticides using enzyme-linked immuno-sorbant assay (ELISA) as a cost-saving screen to determine the efficacy of further sampling.

Monitoring will also consist of field measurements for pH, conductivity and temperature using Oakton pH/Con 10 pH/Conductivity/Temperature meters.

6.3 Project schedule

Table 2. (Element 6) Project schedule timeline.

Activity	Date (MM/DD/YY)		Deliverable	Deliverable Due Date
	Anticipated Date of Initiation	Anticipated Date of Completion		
Dormant spray monitoring	12/10/2004	3/1/2005	none	
Winter storm sample collection	1/3/2005	3/20/2005	Sample concentration data	Within 4 weeks of sample delivery
Irrigation season sample collection in Delta and San Joaquin River Basin	3/1/2005	5/31/2005	Sample concentration data	Within 4 weeks of sample delivery
Summarize winter storm sampling data	3/1/2005	4/22/2005	Complete data set	5/2/2005
Draft final report	3/20/2005	5/2/2005	Draft final report for review	5/2/2005
Final report	5/16/2005	6/17/2005	Final report	6/17/2005

6.4 Geographical setting

The sampling area encompasses the lower Sacramento and Feather rivers to the north (Figure 2), the Sacramento-San Joaquin Delta around Stockton and north of Rio Vista (Figure 3), and the lower Stanislaus, San Joaquin, Tuolumne and Merced rivers to the south (Figure 4). The northern and westernmost site is the Sacramento River at Colusa. The southern and easternmost site is the Merced River near Newman.

Figure 2. The six sampling sites in the Sacramento River Basin to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05.

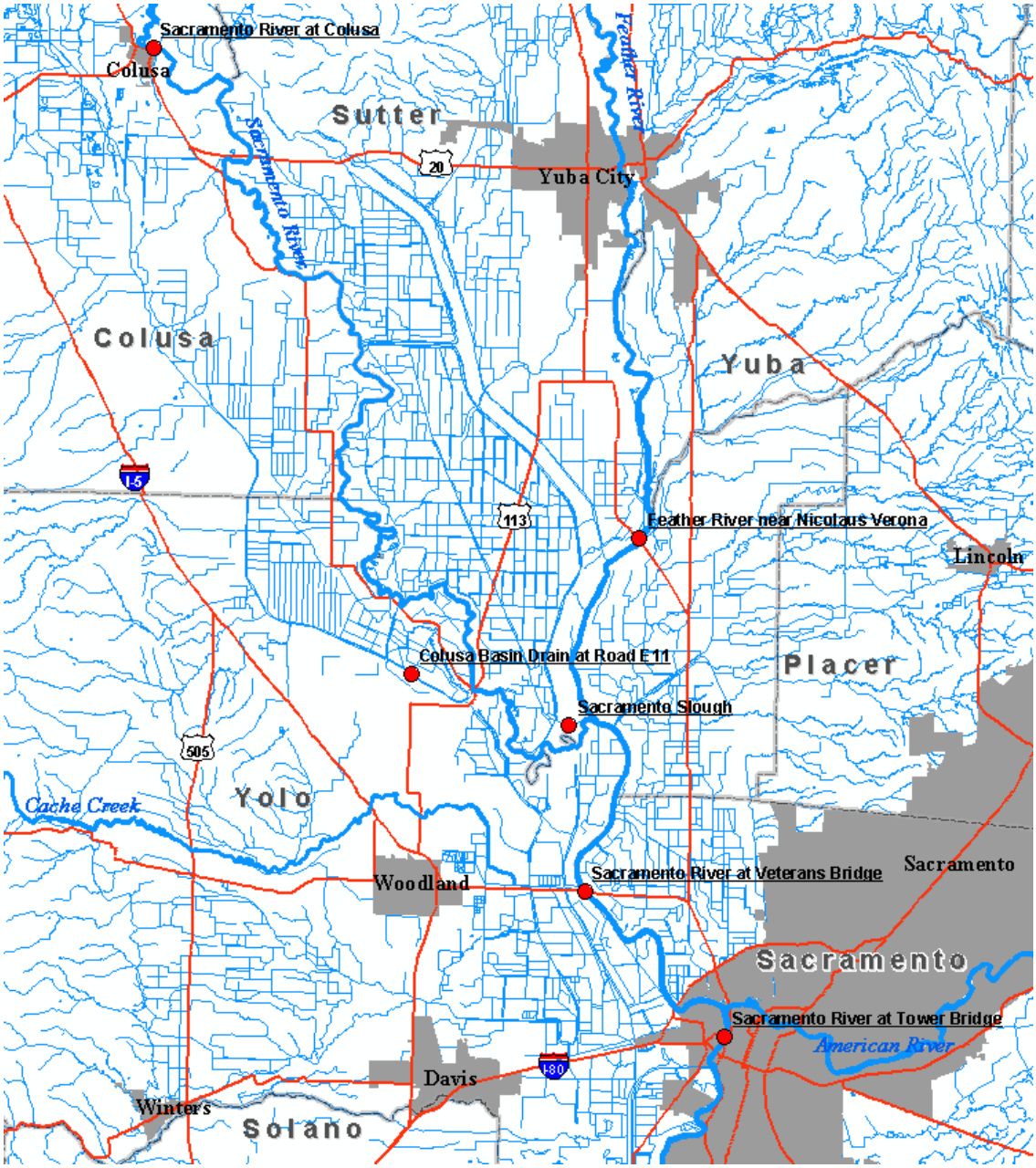


Figure 3. The seven sampling sites in the Sacramento-San Joaquin Delta to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05.

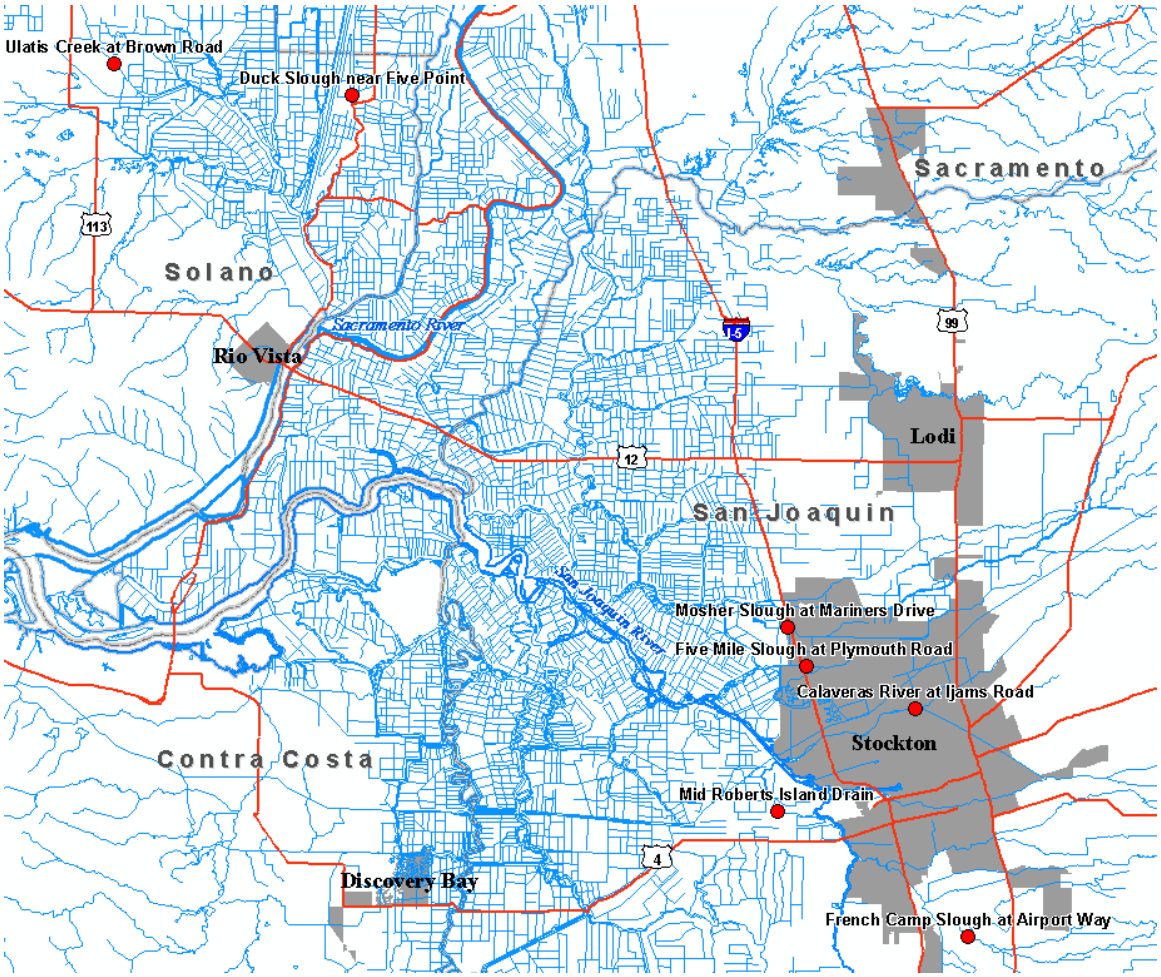
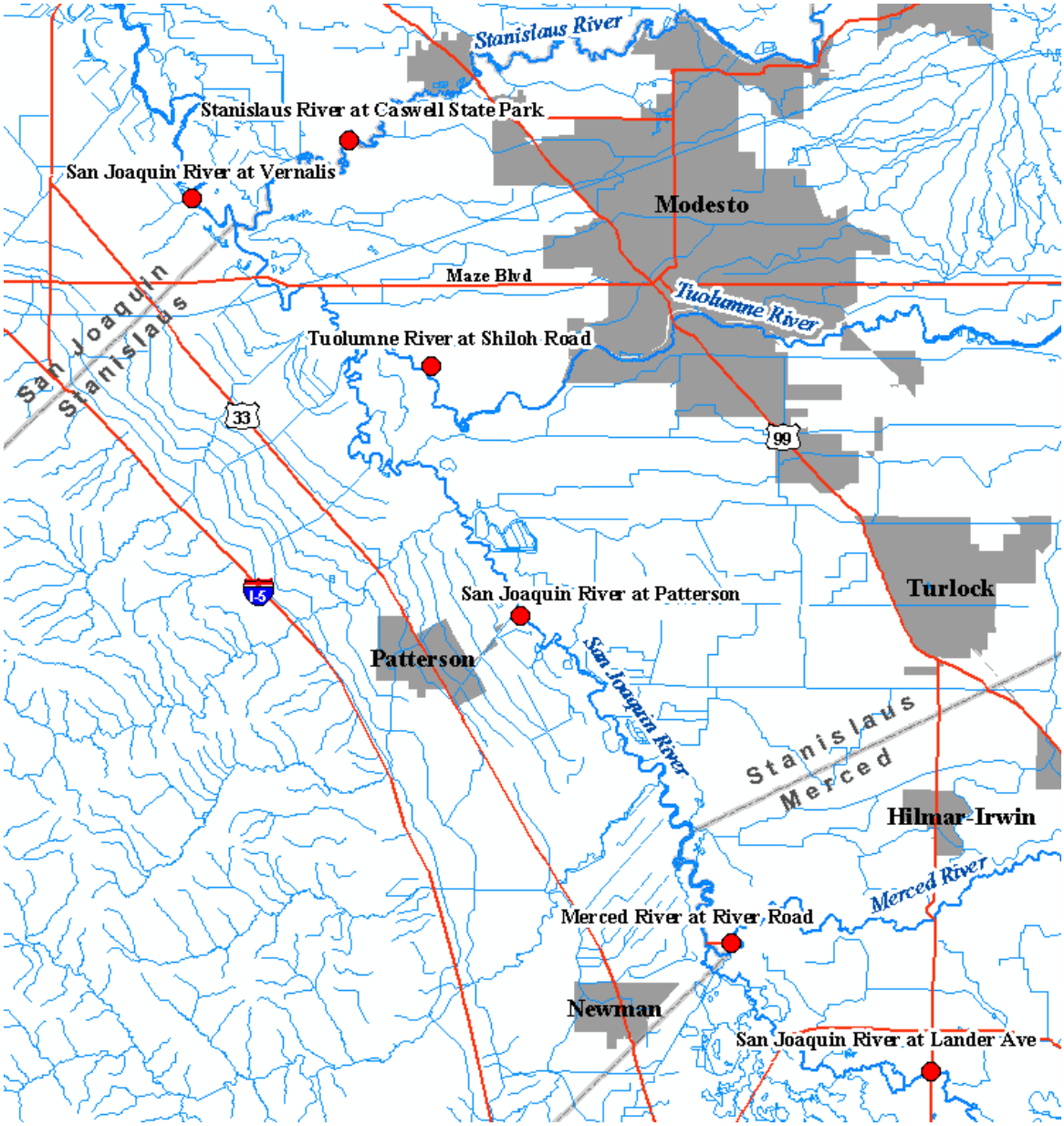


Figure 4. The six sampling sites in the San Joaquin River Basin to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05.



6.5 Constraints

Calculated loads of pesticides are based on the collection of 1-2 samples per day at each site and therefore, are only a best estimate of what is actually moving through each system based on a limited number of samples. Storm intensity and duration affect the rate of pesticide runoff. In extreme wet weather conditions runoff of pesticides may occur so rapidly that accurate estimates of pesticide loads are not possible to obtain.

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7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Field and Laboratory Measurements Data Quality Objectives Tables

Table 3. (Element 7) Data quality objectives for field measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limit	Completeness
Field Testing	Temperature	± 0.5 °C	± 0.5 °C	NA	NA	90%
	Electrical Conductivity	± 5%	± 5%	NA	NA	90%
	pH	± 0.5 units	± 0.5 units	NA	NA	90%
Field Test Kit	ELISA	± 25%	± 20%	± 20%	20 ng/L	90%

Table 4. (Element 7) Data quality objectives for laboratory measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Organophosphate pesticides	Diazinon	Standard Reference Materials (diazinon) within 95% CI stated by provider of material.	Field replicate or MS/MSD ± 25% RPD. Field replicate minimum.	Matrix spike 70% - 130% or control limits at ± 3 standard deviations based on actual lab data.	0.020 ppb	90%
	Chlorpyrifos	Standard Reference Materials (chlorpyrifos) within 95% CI stated by provider of material.	Field replicate or MS/MSD ± 25% RPD. Field replicate minimum.	Matrix spike 70% - 140% or control limits at ± 3 standard deviations based on actual lab data.	0.010 ppb	90%

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

All staff performing field or laboratory procedures shall receive training from the AEAL Quality Assurance Officer, Melissa Turner, to ensure that the work is conducted correctly and safely. At a minimum, all staff shall be familiar with the field guidelines and procedures and the laboratory SOP included in this QAPP. All staff/students conducting fieldwork must have completed the 4-hour Field Safety Training course administered by the SWRCB and the Drivers Safety Training Course administered by UC Davis. All work shall be performed under the supervision of experienced staff or a field coordinator. A copy of the staffs' training records will be filed in each specific project file.

8.2 Training and certification documentation.

Field staff training is documented and filed in the UC Davis Aquatic Ecosystems Analysis Laboratory (AEAL) office in Davis, CA. Documentation consists of a record of the training date, instructor, whether initial or refresher, and whether the course was completed satisfactorily.

AEAL maintains records of its training. Those records can be obtained if needed from the AEAL Quality Assurance Officer, Melissa Turner.

8.3 Training personnel.

All project staff will attend the 4-hour Field Safety Training Course given by Vera Liou of the SWRCB on December 23 at the AEAL office in Davis, CA. The Drivers Safety Training Course will be provided to all project staff by a representative of the UC Davis Fleet Services on December 20 in the AEAL office in Davis, CA.

Table 5. (Element 8) Specialized personnel training or certification.

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/ Organizational Affiliation	Location of Records & Certificates
Field Safety Training	Vera Liou, SWRCB	All UCD and SWRCB sampling staff	AEAL office
Drivers Safety Training	Bob Jahn, UC Davis	All UCD and SWRCB sampling staff	AEAL office

9. DOCUMENTS AND RECORDS

AEAL will collect records for sample collection, field analyses, and laboratory analysis. Samples sent to the CDFA Center for Analytical Chemistry will include a Chain of Custody form. AEAL generates records for sample receipt and storage, analyses, and reporting.

AEAL has an existing database of field measurements from previous studies. The Project Supervisor, Henry Calanchini, maintains this database. Mr. Calanchini will also maintain the database of information collected in this project.

All records generated by this project will be stored at AEAL's main office. CDFA records pertinent to this project will be maintained at CDFA's main office. Copies of all records held by CDFA will be provided to AEAL and stored in the project file.

Copies of this QAPP will be distributed to all parties involved with the project, including field collectors and the AEAL in-house laboratory analyst. Copies will be sent to the CDFA Manager for distribution within the CDFA. Any future amended QAPPs will be held and distributed in the same fashion. All originals, and subsequent amended QAPPs, will be held at the CVRWQCB. Copies of versions, other than the most current, will be discarded so as not to create confusion.

Persons responsible for maintaining records for this project are as follows. Henry Calanchini, Project Supervisor will maintain all sample collection, sample transport, chain of custody, and field analyses forms. Stephen Siegel, CDFA laboratory manager will maintain all records associated with the receipt and analysis of samples analyzed for organophosphate pesticides. Henry Calanchini will maintain the database; data management procedures including back-up plans for data stored electronically are outlined in Element 19 of this QAPP. Dr. Mark Lee, Laboratory Director for CDFA will maintain CDFA's records. CVRWQCB Project Manager Danny McClure will oversee the actions of these persons and will arbitrate any issues relative to records retention and any decisions to discard records.

All records will be passed to the Regional Board Project Manager, Danny McClure, at project completion. Copies of the records will be maintained at AEAL and CDFA for five years after project completion then discarded, except for the database, which will be maintained without discarding.

A final data report will be prepared containing the data collected for the TMDL program from April of 2004 through March 2005, and summarizing the activities conducted to generate that data – including sample collection, storage and analysis. The data report will contain, as an appendix, a CD containing, in tabular format, all data generated during this project, as well as the diazinon and chlorpyrifos load estimates for all sites and sampling times for which concentration and flow data are available. The report will also include the results of the analysis of QC samples, and an assessment of the overall quality of the data generated in comparison to the goals described in this QAPP.

Table 6. (Element 9) Document and record retention, archival, and disposition information.

	Identify Type Needed	Retention	Archival	Disposition
Sample Collection Records	Chain of Custody	Original with CDFA	Copies with AEAL and CVRWQCB	Stored at the Regional Board for at least 5 years
Field Records	Field Data Sheet	AEAL	AEAL	Stored at AEAL for 5 years
Analytical Records	Excel Sample Reports	CDFA	Copies to AEAL and CVRWQCB	Stored at the Regional Board for at least 5 years
Data Records	Excel database	AEAL	Copy to CVRWQCB	Stored at the Regional Board for at least 5 years
Assessment Records	Draft and Final Data Reports	AEAL	Copy to CVRWQCB	Stored Permanently at Regional Board

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GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

Sampling sites within each of the three basins are described in their respective monitoring plans (Appendices 1a, 1b & 1c). Locations for pesticide monitoring were selected by Regional Board staff on the basis of documented use of organophosphate pesticides upstream from the locations monitored, on pesticide-caused toxicity detected at these streams/rivers, and on inclusion of pesticides on the 303(d) list of impaired water bodies. The specific sampling site selection criteria for each basin are as follows:

In the Sacramento Basin sampling sites were selected to assess progress in meeting the water quality objectives for diazinon in the Sacramento and Feather Rivers, and the load allocations set in the Sacramento and Feather River diazinon TMDL for the Colusa Basin, Butte Sutter Basin, Sacramento River above Colusa, the Feather River, and the discharges into the Sacramento River Between Verona and I Street in the City of Sacramento.

Sites in the Delta were selected to monitor pesticide concentrations in mainstem rivers, back sloughs, agricultural drains, and urban areas. Mosher Slough (Delt02) and Five Mile Slough (Delt03) are in back sloughs of urban areas; Mid Roberts Island Drain (Delt05) and Duck Slough (Delt11) are in main drains of agricultural fields; and the remaining sites are in back sloughs that drain primarily agricultural areas. In addition, the selected sites also include the boundaries and interior of the Delta. Calaveras River (Delt04), French Camp Slough (Delt06), and Ulatis Creek (Delt10) are located near, or at the Delta boundary. The other sites are within the Delta. Additional sites were monitored in 2002, and 2003 but were removed from the sampling plan due to low concentrations of pesticides detected.

In the San Joaquin River Basin sampling sites were selected:
1) to represent the three major tributaries (Merced, Stanislaus and Tuoloumne) near their confluences with the mainstem San Joaquin River.
2) the mainstem site at Vernalis was selected to represent the furthest downstream (integrator) site
3) The San Joaquin River at Patterson and the San Joaquin River at Lander Avenue were selected to represent different reaches of the mainstem river. Monitoring of these sites has varied, depending on available funding.

In the event that a site becomes inaccessible or unsafe to sample for any reason an alternative sampling site for the affected waterbody will be scouted by sampling personnel. Sampling personnel will notify the AEAL Project Supervisor of the alternative site and any conditions which may influence the quality of a sample collected at the site. The AEAL Project Supervisor will then seek permission from the Regional Board Project Manager to collect a sample at the alternative site.

Because the sampling sites are in predetermined locations, and the sampling personnel are assigned specific sites for the duration of this project, the natural variability of the sampling process is limited to the time at which the samples are collected and localized soil conditions and weather patterns. The concentration of target pesticides will fluctuate on a temporal basis at each sampling site depending upon the rate at which pesticide runoff occurs, the amount of pesticide entering the subject water body, distance the pesticide has traveled from its source, the speed at which it travels and the volume of water passing by that point. The saturation level of soils affects the rate of pesticide runoff. More rainfall is required to generate runoff when soil conditions are dry then when soil has been saturated from previous rainfall or irrigation. Localized weather patterns affect the rate of pesticide runoff with heavy rainfall generating faster runoff than light rain.

Factors that could bias contaminant levels found in the samples include poor sampling techniques and improper cleaning of equipment as well as limited access to parts of the channel. These sources of bias can be avoided through strict adherence to the methods described in Element 11and Appendices 3a, 3b and 3c.

11. SAMPLING METHODS

At sites where a bridge is present samples will be collected by lowering a 3L Teflon® bottle in a weighted cage at three equally spaced intervals across the width of the stream channel. At each vertical the bottle will be filled ¼ full. After collecting the three verticals the 3L bottle will be capped, agitated to ensure thorough mixing, and poured into a pre-labeled 1L amber glass bottle.

At the Tower Bridge site, and the boat sites, samples will be collected with a USGS D77 velocity-integrated sampler with a 3L Tefllon® bottle using the equal-width increment method (EWI) from the USGS National Field Manual Section 4.1.1.A Isokinetic, Depth-Integrated Sampling Methods (Wilde, F.D., et al 1999).
Each sample will be a composite of 6-10 verticals evenly spaced across the stream channel. The sample from each vertical will be mixed in a stainless steel splitter and a single sample will be poured from the splitter into a pre-labeled 1L amber glass bottle.

At all other sites grab samples will be collected using a pole sampler from as near to the center of the channel as possible. Regardless of collection method all samples will be poured into Fisher Scientific 300 Series certified pre-cleaned 1L amber glass bottles. The bottles will be filled so that no headspace remains prior to capping. All samples will be immediately placed on ice, in coolers, and preserved at 4° C until delivery to the CDFA lab.

At sites in the Sacramento basin an additional 250ml sample will be collected using the methods and preservation detailed above. Each 250ml sample will be analyzed at the AEAL lab using Enzyme-Linked Immunosorbent Assay (ELISA). The results from these samples will be used as a screen to determine the presence or absence of diazinon and whether to deviate from the original sampling schedule.

For further details on sampling methods please see the sample collection SOP's attached to the monitoring plans in Appendices 3a, 3b and 3c.

Table 7. (Element 11) Sampling locations and sampling methods.

Sampling Location	Location ID Number	Matrix	Analytical Parameter	# Samples (include field duplicates, field blanks and matrix spikes)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Sacramento River at Colusa	11389500	Water	Organophosphate pesticides	17	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Sacramento River at Tower Bridge	383430121302001	Water	Organophosphate pesticides	18	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Colusa Basin Drain Near Knights Landing	11390890	Water	Organophosphate pesticides	17	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Sacramento River at Veterans Bridge	384027121373401	Water	Organophosphate pesticides	18	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Feather River near Nicolaus/Verona	384752121375301	Water	Organophosphate pesticides	17	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Sacramento Slough	384649121381101	Water	Organophosphate pesticides	19	Appendix 3a	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Mosher Slough at Mariners Drive	Delt02	Water	Organophosphate pesticides	16	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Five-Mile Slough at Plymouth Road	Delt03	Water	Organophosphate pesticides	17	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Calaveras River at Ijams Road	Delt04	Water	Organophosphate pesticides	17	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days

Table 7. (Element 11) Sampling locations and sampling methods *(continued)*.

Sampling Location	Location ID Number	Matrix	Analytical Parameter	# Samples (include field duplicates, field blanks and matrix spikes)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Mid Roberts Island Drain	Delt05	Water	Organophosphate pesticides	26	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
French Camp Slough at Airport Road	Delt06	Water	Organophosphate pesticides	25	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Ulatis Creek at Brown Road	Delt10	Water	Organophosphate pesticides	26	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Duck Slough	Delt11	Water	Organophosphate pesticides	25	Appendix 3b	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
San Joaquin at Vernalis	11303500	Water	Organophosphate pesticides	27	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Stanislaus River at CSP	374209121103800	Water	Organophosphate pesticides	27	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Tuolumne River at Shilo Road	11290200	Water	Organophosphate pesticides	27	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
San Joaquin River at Lander Avenue	11260815	Water	Organophosphate pesticides	5	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
San Joaquin River at Patterson	11274570	Water	Organophosphate pesticides	10	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days
Merced River at River Road	11273500	Water	Organophosphate pesticides	15	Appendix 3c	1L	1L Amber glass bottles, Fisher Scientific 300 series	Ice	7 Days

12. SAMPLE HANDLING CUSTODY

Once sample containers are filled they are labeled and stored on ice for transport to the CDFA laboratory. ELISA samples will be stored on ice and transported to the AEAL Laboratory. Sample containers will be Fisher Scientific 300 Series certified pre-cleaned 1L and 250 ml amber glass bottles for environmental and ELISA samples respectively.

Samples are delivered as follows. Environmental samples are delivered to the CDFA lab on the day of collection or the following day. If samples are to be delivered the following day they will be kept in a secure space at the AEAL. ELISA samples will be delivered to the AEAL Laboratory for analysis. Sample holding times are as follows. Samples may be kept at 4° C, in the dark, for up to 7 days. Extraction must be performed within the 7 days of the time of sample collection.

Table 8. (Element 12). Sample handling and custody.

Parameter	Container	Volume	Initial Preservation	Holding Time
organophosphate pesticides	Fisher Scientific 300 Series amber glass bottle	1L	ice	7 days
organophosphate pesticides	Fisher Scientific 300 Series amber glass bottle	250ml	ice	7 days

No special handling or custody procedures are needed. The chain of custody form is used as a shipping record.

Samples may be disposed of when analysis completed and all analytical quality assurance/quality control procedures are reviewed and accepted

Each sample will be documented on a chain of custody form at the time of collection. The chain of custody will remain with the samples at all times. When the samples are delivered to the lab the sampler will relinquish custody by signing the appropriate space on the chain of custody form. The lab attendant will accept custody by signing the appropriate space on the chain of custody form. The lab attendant will make a copy of the chain of custody form and give it to the sampler for filing at the AEAL office.

The following page contains an example of a TMDL monitoring chain of custody form.

Aquatic Ecosystems Analysis Laboratory
John Muir Institute of the Environment
University of California, Davis
1490 Drew Avenue, Suite 150
CA 95616

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION
11020 Sun Center Drive # 200 Rancho Cordova, CA
PHONE: (916) 464 3291

CHAIN OF CUSTODY

Program:	Project Name:	Preservative	HOW COLLECT						ANALYSIS REQUIRED			
Sac TMDL Unit	Sacramento TMDL 2003/2004											
Sampler (Name):	Sampler (Signature):											

SAMPLE INFORMATION				CONTAINER		SAMPLE TYPE																
IDENTIFICATION	LOCATION	DATE	TIME	TYPE	NO.	BA	TOX_1	TOX_2	SW			INTEGRATED GRAB	GRAB	AUTO SAMPLER		TOTAL	DISSOLVED		ELISA	GC	GC/MS	
				1L					x	ice						x					x	
				1L					x	ice						x					x	

SPECIAL INSTRUCTIONS / SUSPECTED CONSTITUENTS:	Contact Name and Number:
Diazinon and Chlorpyrifos	

RELINQUISHED BY (Signature) DATE/TIME	RECEIVED BY (Signature)	RELINQUISHED BY (Signature)	RECEIVED BY (Signature)
RELINQUISHED BY (Signature) DATE/TIME	RECEIVED BY (Signature)	RELINQUISHED BY (Signature)	RECEIVED BY (Signature)

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13. ANALYTICAL METHODS

See Tables 9 and 10 for analytical methods

Table 9. (Element 13) Field analytical methods.

Analyte	Laboratory / Organization	Project Action Limit (units, wet or dry weight)	Project Quantitation Limit (units, wet or dry weight)	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs (1)	Method (1)
pH	Field monitoring by AEAL field staff	none	±0.01 pH	Appendix 5	None		
Conductivity	Field monitoring by AEAL field staff	none	0.01 mS	Appendix 5	None		
Temperature	Field monitoring by AEAL field staff	none	0.1ºC	Appendix 5	None		

(*) *Standard Methods for the Examination of Water and Wastewater*, 20th edition.

Table 10. (Element 13) Laboratory analytical methods.

Analyte	Laboratory / Organization	Project Action Limit (units, wet or dry weight)	Project Quantitation Limit (units, wet or dry weight)	Analytical Method		Achievable Laboratory Limits	
				Analytical Method/ SOP	Modified for Method yes/no	MDLs (1)	Method (1)
Diazinon	AEAL In-house laboratory	20 ng/L	20 ng/L	ELISA/ no SOP	None		
Diazinon	CDFA	0.007 µg/L	0.020 µg/L	GC-MS/SOP: Appendix 6	No	0.007 µg/L	Appendix 6
Chlorpyrifos	CDFA	0.004 µg/L	0.010 µg/L	GC-MS/SOP: Appendix 6	No	0.004 µg/L	Appendix 6

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14. QUALITY CONTROL

Internal quality control (QC) is achieved by analyzing a series of duplicate, blank, spike and spike duplicate samples to ensure that analytical results are within the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that the data of known quality are produced and documented. The quality control assessments used in the TMDL monitoring program are discussed below. Quality control acceptance limits and frequencies are summarized in Tables 11 and 12 and Appendices 2a, 2b & 2c. Detailed procedures for preparation and analysis of quality control samples are provided in the analytical method document in Appendix 6.

14.1 Data Quality Objectives and Quality Assurance Objectives

Data Quality Objectives (DQOs) and Quality Assurance Objectives (QAOs) are related data quality planning and evaluation tools for all sampling and analysis activities. A consistent approach for developing and using these tools is necessary to ensure that enough data are produced and are of sufficient quality to make decisions for this study.

DQOs and Data Use Planning
DQOs specify the underlying reason for collection of data, data type, quality, quantity, and uses of data collection. For this program, data is needed for identification of sources and evaluation of management practices effectiveness.

Data Quality Category
For this study, definitive data using standard US Environmental Protection Agency (EPA) or other reference methods are performed by the California Department of Food and Agriculture with Regional Board staff approval. Data are analyte-specific. These methods have standardized QC and documentation requirements, providing supporting information necessary to verify all reported results.

Quality Assurance Objectives (QAOs)
Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, comparability and completeness (PARC). The QAOs presented in this QAPP represent the minimum acceptable specifications that should be considered routinely for field and analytical procedures. The QAOs are then used as comparison criteria during data quality review by the Regional Board to determine if the minimum requirements have been met and the data may be used as planned.

14.2 Development of Precision and Accuracy Objectives

Laboratory control spikes (LCSs) are used to determine the precision and accuracy objectives. LCSs are fortified with target compounds to monitor the laboratory precision and accuracy.

Field duplicates measure sampling precision and variability for comparison of project data. Acceptable relative percent difference (RPD) is less than 25 for field duplicate analyses. If field duplicate sample results vary beyond these objectives, the results are further evaluated to identify the cause of the variability. The precision and accuracy objectives for this QAPP are listed in Table 4.

14.3 Precision Accuracy Representativeness Completeness (PARC) Definitions and Calculations

Precision
Precision measures the reproducibility of repetitive measurements. Precision is evaluated by calculating the RPD between duplicate spikes, duplicate sample analyses or field duplicate samples and comparing it with appropriate precision objectives established in this QAPP. Analytical precision is developed using repeated analyses of identically prepared control samples. Field duplicate samples analyses results are used to measure the field QA and

matrix precision. Interpretation of precision data must include all possible sources of variability. The precision objectives for this QAPP are listed in Table 4.

The **M**ean of the **A**bsolute value of single or aggregated **R**elative **P**ercent **D**ifference (MARPD) is used to express precision and is calculated as shown below:

$$MARPD = \frac{1}{k}\sum_{j=1}^{k}\left(\frac{|S1 - S2|}{S1 + S2}\right)_j \times 200$$

Where: S1 = The value for the primary sampler,
S2 = The value for the collocated sampler, and
k = The number of pairs of valid data.

For reporting purposes, the absolute value of the relative percent difference is used when a single pair is evaluated and referred to simply as ARPD or RPD. The formula shown above then reduces to:

$$RPD = \left(\frac{|S1 - S2|}{S1 + S2}\right) \times 200$$

Note: Signed results (positive and negative) are not generally used for reporting.

Accuracy

Accuracy measures correctness, or how close a measurement is to the true or expected value. Accuracy is measured by determining the percent recovery of known concentrations of analytes spiked into field sample or reagent water before extraction. The stated accuracy objectives for Laboratory control spikes or matrix spikes should reflect the Qualitative Objectives anticipated concentrations and/ or middle of the calibration range. The accuracy objectives for this QAPP are listed in Table 4. Accuracy can be calculated with the following formula:

$$\%R = \left[1 + \left(\frac{Y - X}{X}\right)\right] \times 100$$

Where: %R = Percent recovery. The amount measured as compared to the "true" value, expressed as a percentage,
Y = The measured value, and
X = The true value.

Representativeness

Representativeness is obtained by using standard sampling and analytical procedures listed and referenced in this QAPP to generate data that are representative of the sites. The representativeness objectives for this QAPP are listed in Table 4.

Comparability

The comparability of data produced by and for this program is predetermined by the commitment of its staff and contracted laboratories to use standardized methods, where possible, including EPA-approved analytical methods, or documented modifications thereof which provide equal or better results. These methods have specified units in which the results are to be reported.

Measurements are made according to standard procedure, or documented modifications thereof which provide equal or better results, using common units such as Celsius, feet, feet/sec, mg/L, µg/L, mg/kg, etc. Analytical procedures are set by the USEPA approval list published in 40 CFR 136 (USEPA 2004(a)).

Completeness

Completeness is calculated for each method and matrix for an assigned group of samples. Completeness for a data set is defined as the percentage of unqualified and estimated results divided by the total number of the data points. This represents the usable data for data interpretation and decision-making. Completeness does not use results that are qualified as rejected or unusable, or that were not reported as sample loss or breakage. The overall objective for completeness is 90% for this project (Table 4). Completeness can be calculated with the following formula:

$$\%C = \left[1 + \left(\frac{Y - X}{X}\right)\right] x100$$

Where: %C = Percent completeness
Y = The number of valid data points, and
X = The total possible number of data points.

14.4 Field Quality Control

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity. For basic water quality analyses, quality control samples to be prepared in the field will consist of field blanks, field duplicates and matrix spikes (when applicable). The number of field duplicates and field blanks are set to achieve an overall rate of at least 5% of all analyses for a particular parameter. The external QA samples are rotated among sites and events to achieve the overall rate of 5% field duplicate samples and 5% field blanks (as appropriate for specific analyses). The frequency and acceptance limits of field quality control samples for this project are listed in Table 11.

Field Blanks

The purpose of analyzing field blanks is to demonstrate that sampling procedures do not result in contamination of the environmental samples. Field blanks will be prepared and analyzed for all analytes of interest at the rate of one per sample event, along with the associated environmental samples. Field blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples. If any analytes of interest are detected at levels greater than the Reporting Limit (RL) for the parameter, the sampling crew should be notified so that the source of contamination can be identified (if possible) and corrective measures taken prior to the next sampling event. If the concentration in the associated samples is less than five times the value in the field blank, the results for the environmental samples may be unacceptably affected by contamination and should be qualified as below detection at the reported value.

Field Duplicates

The purpose of analyzing field duplicates is to demonstrate the precision of sampling and analytical processes. Field duplicates will be prepared at the rate of one per sampling event, and analyzed along with the associated environmental samples. Field duplicates will consist of two aliquots from the same composite sample, or of two grab samples collected in rapid succession. If an RPD greater than 25% is confirmed by reanalysis, environmental results will be qualified as estimated. The sampling crew should be notified so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to the next sampling event.

14.5 Laboratory Quality Control

Laboratory QC is necessary to control the analytical process within method and project specifications, and to assess the accuracy and precision of analytical results. For basic water quality analyses, quality control samples prepared in the contract laboratory (s) will typically consist of equipment blanks, method blanks, laboratory control samples, laboratory duplicates and surrogate added to each sample (organic analysis).
The frequency and acceptance limits of laboratory quality control samples for this project are listed in Table 12.

Equipment Blanks
The purpose of analyzing equipment blanks (EB) is to demonstrate that sampling equipment is free from contamination. Prior to using sampling equipment for the collection of environmental samples, the laboratory responsible for cleaning and preparation of the equipment will prepare bottle blanks and sampler blanks. These will be prepared and analyzed at the rate of one each per piece of sampling equipment. The blanks will be analyzed using the same analytical methods specified for environmental samples. If any analytes of interest are detected at levels greater than the MDL, the source(s) of contamination should be identified and corrected, the affected equipment should be re-cleaned, and new equipment blanks should be prepared and analyzed. Sampler blanks will consist of laboratory-prepared blank water processed through the sampling equipment using the same procedures used for environmental samples.

Method Blanks
The purpose of analyzing method blanks is to demonstrate that the analytical procedures do not result in sample contamination. Method blanks (MB) will be prepared and analyzed by the contract laboratory at a rate of at least one for each analytical batch. Method blanks will consist of laboratory-prepared blank water processed along with the batch of environmental samples. If the result for a single MB is greater than the acceptance limits the source(s) of contamination should be corrected and the associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as below detection at the reported blank value.

Laboratory Control Samples
The purpose of analyzing laboratory control samples (LCS) is to demonstrate the accuracy of the analytical method. Laboratory control samples will be analyzed at the rate of one per sample batch. Laboratory control samples will consist of laboratory fortified method blanks. If recovery of any analyte is outside the acceptable range for accuracy, the analytical process is not being performed adequately for that analyte. In this case, if the matrix spikes are also outside the acceptable range, the LCS and associated samples should be reanalyzed. If reanalysis is not possible, the associated sample results should be qualified as low or high biased.

Matrix Spikes and Matrix Spike Duplicates
The purpose of analyzing matrix spikes and matrix spike duplicates is to demonstrate the performance of the analytical method in a particular sample matrix. The number of matrix spikes are set to achieve an overall rate of at least 5% of all analyses for a particular parameter. Each matrix spike and matrix spike duplicate will consist of an aliquot of laboratory-fortified environmental sample. Spikes concentrations should be added at five to ten times the .reporting limit for the analyte of interest. If matrix spike recovery of any analyte is outside the acceptable range, the results for that analyte have failed the acceptance criteria. If recovery of laboratory control samples is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. Attempt to correct the problem (by dilution) and re-analyze the samples and the matrix spikes. If the matrix problem can't be corrected, qualify the results for that analyte as appropriate (low or high biased) due to matrix interference. If the matrix spike duplicate RPD for any analyte is greater than the precision criterion, the results for that analyte have failed the acceptance criteria. If the RPD for laboratory duplicates is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution, concentration, etc.) and re-analyze the samples and the matrix spike duplicates. If the matrix problem can't be corrected, qualify the results for that analyte as not reproducible, due to matrix interference. Tables 11 and 12 present the QC requirements for water quality samples at specific criteria.

Table 11. (Element 14) Sampling (Field) QC.

Matrix: water	
Sampling SOP: Appendices 2a, 2b, 2c	
Analytical Parameter(s): diazinon, chlorpyrifos	
Analytical Method/SOP Reference: Appendix 6	
# Sample locations: 19	

Field QC	Frequency/Number per sampling event	Acceptance Limits
Equipment Blanks	One time per each piece of equipment for first event only	Less than Reporting Limit
Field Blanks	Approximately 5%	Less than Reporting Limit
Cooler Temperature	Measured by analyzing lab at time of delivery	$\leq$ 4° C
Field Duplicate Pairs	20	RPD $\leq$ 25%

Table 12. (Element 14) Analytical QC.

Matrix: water	
Sampling SOP: Appendices 2a, 2b, 2c	
Analytical Parameter(s): diazinon, chlorpyrifos	
Analytical Method/SOP Reference: Appendix 6	
# Sample locations: 19	

Laboratory QC	Frequency/Number	Acceptance Limits
Method Blank	1/batch	80-125% All target analytes below reporting limit
Instrument Blank	After any standards	All target analytes below reporting limit
Matrix Spike	18	70-130 % diazinon; 70-140% chlorpyrifos
Matrix Spike Duplicate	18	70-130 % diazinon; 70-140% chlorpyrifos RPD $\leq$ 25%
Lab. Control sample	1/Batch	80-125%
Surrogates	In all samples and QC	80-125%
Internal Standards	All samples and standards	50 – 200 %

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Field measurement equipment will be checked for operation in accordance with the manufacturer's specifications. This includes battery checks, routine replacement of membranes and cleaning of conductivity electrodes on multi-parameter meters, and performance of spin tests, oiling and pivot adjustment on AA type current meters. Equipment will be inspected when first handed out and when returned from use for damage. Spare parts, including additional bolts, nuts, washers and other hardware for sampling equipment, are kept in AEAL sampling vehicles to be accessed during sampling if needed. Additional spare parts are kept at AEAL storage facilities and restocked as needed. AEAL maintains its equipment in accordance with its SOPs, which include procedures specified by the manufacturer and those specified by the method. See Table 13 for deficiency actions corresponding to sampling equipment. See SOP's in Appendices 4 & 5 for documentation of calibration.

Table 13. (Element 15) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
Oakton pH/CON 10 Multi-parameter meter	Rinsing of probe and electrode cleaning	AEAL sampling crews	One time per month If calibration fails calibrate and use backup meter	Appendix 5
USGS Price Type AA current meter	spin test, clean and oil	AEAL sampling crews	spin test before each use (min. 120 seconds) oil and adjust pivot if spin test fails	Appendix 4
Agilent /HP 6890/5973 GC-MSD	Injector cleaning	CDFA Chemists	As needed	Appendix 7
Buchi rotary evaporator	Rinsing condenser	CDFA Chemists	Before each sample	Appendix 8

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

This section briefly describes analytical methods and calibration procedures used at the CDFA laboratory for samples that will be collected under this project. The method listed below can be found in **Appendix 6:** *Multi-Residue Method for Extraction and Analysis of Pesticides in Surface Water*

Method calibration
Five levels of standards are prepared in matrix of reagent grade water to calibrate the analysis method. A linear regression is used including 0,0. The R squared value should be greater or equal to 0.99. Standards are run with the sample set to check for calibration integrity. Continuing calibration standard values should be within ±25% of calibration. Residue concentration is taken from instrument report table and calculated. If the residue amount falls outside the calibration curve, the sample will be diluted and reanalyzed.

$$\text{Residue Amt (ppt)} = \frac{(\text{Instrument amt} \times 500\text{g})}{\text{Weight of sample}}$$

If R squared value of calibration curve is < 0.99, the pesticide level may be determined by direct comparison of residue response to the average response of the nearest bracketing standard concentration. Response of bracketing standards should not vary more than 25%. The residue response should fall within ±30% of standard response. If the residue amount falls outside calibration curve, the sample will be diluted and reanalyzed. A non-linear calibration may be necessary to achieve low detection limits or address specific instrumental techniques. Non-linear calibration is not to be used to compensate for detector saturation or to avoid instrument maintenance.

Calculation using single point comparisons:

$$\text{Sample amt (ppt)} = \left(\frac{\text{Sample response}}{\text{Avg response of bracketing stds}}\right) \times \left(\frac{500\text{g}}{\text{Weight of sample (g)}}\right) \times \text{Std amt}$$

Surrogate: Chlorpyrifos methyl- 500ppt

Table 14. (Element 16) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Oakton pH/CON 10 Multi-parameter meter	Appendix 5	calibrated for pH and electrical conductivity against manufacturer standards	prior to each sampling event	AEAL sampling crew
6890/5973MSD	Appendix 6	5-point initial calibration	Beginning of each analytical run	CDFA Chemist

17. Inspection/Acceptance of Supplies and Consumables

Gloves, sample containers, and any other consumable equipment used for sampling will be inspected by the sampling crew on receipt and will be rejected/returned if any obvious signs of contamination (torn packages, etc.) are observed. Inspection protocols and acceptance criteria for laboratory analytical reagents and other consumables are documented in the CDFA Quality Assurance Manual (Cusick 2004). The laboratory QA Manual is available for review at the CDFA laboratory.

Table 15. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Solvents	Use in extraction of reagent water	No target analytes above Reporting Limit	1/batch	CDFA Chemist
Na_2SO_4	Use in extraction of reagent water	No target analytes above Reporting Limit	1/batch	CDFA Chemist
NaCl	Use in extraction of reagent water	No target analytes above Reporting Limit	1/batch	CDFA Chemist
CH_2Cl_2	Use in extraction of reagent water	No target analytes above Reporting Limit	1/batch	CDFA Chemist

18. Non-Direct Measurements (Existing Data)

The only non-direct measurements are from the AEAL's database of data from prior studies. The database is maintained in accordance with AEAL policy as stated earlier. The data will be reviewed against the data quality objectives stated in section 7 and only that data meeting all of the criteria will be used in this project.

19. Data Management

Data will be maintained as established in section 9 above. Copies of field logs, copies of chain of custody forms, original preliminary and final lab reports, and electronic media reports will be sent to the Regional Board Project Manager . The field crew will retain original field logs. The contract laboratory will retain original chain of custody forms. The contract laboratory(s) will retain copies of the preliminary and final data reports. Henry Calanchini will maintain the database and all project records in AEAL custody. AEAL project data is stored on a secure server with a four partition memory so that if any one memory partition fails it can be rebuilt from the remaining three. The

server is regularly maintained, and data from the server is backed up weekly, by an AEAL employed computer consultant.

Field data sheets are returned to AEAL after each sampling event, copied and filed by sampling crews. Field data including field descriptions and water quality parameters are entered electronically into the database by sampling crews. Discharge measurement data from the field sheets are used to calculate discharges, entered into the database, and then double-checked for accuracy and completeness by the AEAL QA Officer. Analysis results from the CDFA laboratory are sent to the AEAL lab via electronic data deliverables (EDD). Results, as well as site codes, times and dates are transferred, by sampling crews, from CDFA EDDs into the AEAL TMDL database, with minor format changes. After data transfer and entry procedures are completed for each sample event, the final database will be inspected for transcription errors by the AEAL QA Officer.

In cases where environmental results are less than the quantification limit for a parameter, the results will be reported as "less than" the reporting limit; e.g. an analytical result of 4 µg/L for an analyte with a reporting limit of 5 µg/L will be reported as <5 µg/L.

CDFA data management protocol.

All COC's will be signed by an authorized CDFA employee. The original COC will be maintained in a binder.
All samples and QC samples will be logged into the CDFA database and assigned a unique sample ID number. This unique number will be added to the original COC to link client sample ID and lab sample ID.
Each analytical batch will have an extraction preparation sheet. This sheet will be filed in the binder along with the original COC. All standards and sample results from each analytical run will be printed out for review. After initial review of the raw data a summary report is generated for each sample and QC sample. The printed data and the report summary are then reviewed by the section supervisor or their designee for technical accuracy and completeness and then released to the client. All printed data will be archived for a period of 5 years.
A signed copy of the summary report is added to the binder with the original COC and preparation sheet. A signed copy of the summary report will be given to the Regional Board at the end of the sampling season.
The CDFA database is updated showing that the sample has been completed.

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

Data will be maintained as established in section 9 above. Copies of field logs, copies of chain of custody forms, original preliminary and final lab reports, and electronic media reports will be sent to the Regional Board Project Manager . The field crew will retain original field logs. The contract laboratory will retain original chain of custody forms. The contract laboratory(s) will retain copies of the preliminary and final data reports. Henry Calanchini will maintain the database and all project records in AEAL custody. AEAL project data is stored on a secure server with a four partition memory so that if any one memory partition fails it can be rebuilt from the remaining three. The server is regularly maintained, and data from the server is backed up weekly, by an AEAL employed computer consultant.

Field data sheets are returned to AEAL after each sampling event, copied and filed by sampling crews. Field data including field descriptions and water quality parameters are entered electronically into the database by sampling crews. Discharge measurement data from the field sheets are used to calculate discharges, entered into the database, and then double-checked for accuracy and completeness by the AEAL QA Officer. Analysis results from the CDFA laboratory are sent to the AEAL lab via electronic data deliverables (EDD). Results, as well as site codes, times and dates are transferred, by sampling crews, from CDFA EDDs into the AEAL TMDL database, with minor format changes. After data transfer and entry procedures are completed for each sample event, the final database will be inspected for transcription errors by the AEAL QA Officer.

In cases where environmental results are less than the quantification limit for a parameter, the results will be reported as "less than" the reporting limit; e.g. an analytical result of 4 µg/L for an analyte with a reporting limit of 5 µg/L will be reported as <5 µg/L.

CDFA data management protocol.

All COC's will be signed by an authorized CDFA employee. The original COC will be maintained in a binder.
All samples and QC samples will be logged into the CDFA database and assigned a unique sample ID number. This unique number will be added to the original COC to link client sample ID and lab sample ID.
Each analytical batch will have an extraction preparation sheet. This sheet will be filed in the binder along with the original COC. All standards and sample results from each analytical run will be printed out for review. After initial review of the raw data a summary report is generated for each sample and QC sample. The printed data and the report summary are then reviewed by the section supervisor or their designee for technical accuracy and completeness and then released to the client. All printed data will be archived for a period of 5 years.
A signed copy of the summary report is added to the binder with the original COC and preparation sheet. A signed copy of the summary report will be given to the Regional Board at the end on the sampling season.
The CDFA database is updated showing that the sample has been completed.

Site Management

The AEAL project supervisor will observe field activities to ensure tasks are conducted according to the project specifications. The project supervisor is equipped with a cellular telephone for improved communication among the team members. Decontamination of field equipments will occur at a designated area assigned by the field manager. Access for sites is coordinated through the responsible agencies. This includes obtaining any necessary permits and coordinating with facilities and units where site activities will take place.

21. REPORTS TO MANAGEMENT

Data summary and final reports will be issued by AEAL according to the following table.

Table 16. (Element 21) QA Management Reports.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Complete data set and summary	one time only	5/2/2005	Henry Calanchini	CVRWQCB Project Manager and Technical Reviewers
Draft final report for review	one time only	5/2/2005	Henry Calanchini	CVRWQCB Project Manager and Technical Reviewers
Final report	one time only	6/17/2005	Henry Calanchini	CVRWQCB Project Manager and Technical Reviewers
Statistical Analysis of lab QC's	one time only	5/2/2005	Stephen Siegel	AEAL Project Manager, CVRWQCB Project Manager and Technical Reviewers

Final Report

AEAL, will prepare a report after conducting data validation. The elements described below will be addressed and included in the report:

- Description of the project including the number of samples, analyses, completeness and any significant problems or occurrences that influence data use.
- The QA/QC activities performed during this project.
- QC sample results, type and number of samples including the results that did not meet the project objectives, and the impact on usability.
- Tables of analytical results for usable and unusable data.

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. Data will be separated into three categories: data meeting all data quality objectives, data meeting failing precision or recovery criteria, and data failing to meet accuracy criteria. Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category is considered usable by the project. Data falling in the last category is considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with a "J" as per EPA specifications (USEPA 2004(b)).

In cases where field blank results exceed the acceptance criteria, data collected during the associated sample run will be qualified and reported as follows:

- Measured environmental sample concentrations greater than or equal to 5 times the field blank level will be reported with no qualification.
- Measured environmental sample concentrations less than 5 times the field blank level will be qualified as "less than" the measured value, e.g. if a field blank is equal to 1.5 µg/L, a measured environmental concentration of 4.0 µg/L will be reported as <4.0 µg/L.
- Any data qualifications resulting from QC analyses will be reported with the environmental data as appropriate.

23. VERIFICATION AND VALIDATION METHODS

Laboratory Data Review, Verification and Reporting

The CDFA QA Officer, Stephen Siegel, will use this QAPP for validating the data generated by the laboratory. The laboratory personnel will verify that the measurement process was "in control" (i.e., all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, the CDFA laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

The laboratory analyst performing the analyses is responsible for the reduction of the raw data generated at the laboratory bench to calculate the concentrations.

The analytical process includes verification or a quality assurance review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data (e.g. chromatogram) with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;

- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

Specific Quality Control procedures are documented in the laboratory quality assurance manual. After the data have been reviewed and verified, the laboratory reports are signed for release and distributions. Raw data and supporting documentation is stored in confidential files by laboratory document control.

Only data, which have met data quality objectives, or data, which have acceptable deviations explained will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable.

Data Validation

Data validation (data quality audit) is conducted by the AEAL QA Officer, Melissa Turner, to verify whether an analytical method has been performed according to the method and project specifications, and the results have been correctly calculated and reported. The AEAL will conduct the data validation prior to submitting the data to CVRWQCB. Specific items that are reviewed during data validation are:

- Chain of custody records
- Documentation of the laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

24. RECONCILIATION WITH USER REQUIREMENTS

The diazinon and chlorpyrifos concentration data generated in this project will be used by the Regional Board and others for the assessment of progress in reducing pesticide runoff into surface waters and for the comparison of current concentrations with criteria for the protection of freshwater ecosystems, such as the CDFG criteria listed in Element 5.3. For the Sacramento River basin, the diazinon concentrations in the Sacramento and Feather Rivers and the diazinon loads coming into the Sacramento River from five tributary subwatersheds will be compared to those allowable under the Sacramento and Feather River TMDL (Karkoski et al., 2003).

Data on concentrations of diazinon and chlorpyrifos generated in this study will be of known and documented quality so that regulatory decision makers and other stakeholders will know the relative accuracy of the measurements being used to support comparisons with monitoring data from previous studies, criteria for the protection of freshwater ecosystems, and regulatory requirements. Unless it is otherwise qualified, the diazinon and chlorpyrifos data generated in this project will meet the Quality Assurance Objectives listed in Element 14. The reporting limits for diazinon and chlorpyrifos are below recommended criteria for the protection of aquatic ecosystems listed in Element 5.3, so the measurements will be sensitive enough to detect exceedances of these criteria. The final data report will indicate the level of completeness of the data generated and indicate any times in which data meeting the Quality Assurance Objectives was not obtained. This information can be used along with concentration graphs, mass balances, and other tools to determine how well the data obtained represents the concentrations and loads of diazinon and chlorpyrifos that are present at the sites sampled during storm and irrigation runoff events.

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26. REVISION LOG:

DATE	REVISION #	REASON FOR REVISION	APPROVED BY	DATE
3/29/05	1.0	Appended this Revision Log to QAPP document.		
3/29/05	1.0	Added methylene chloride to Table 15 (Inspection of Supplies and Consumables) in Element 17:		
3/29/05	1.0	Added title to Element 20: Assessments & Response Actions		
3/29/05	1.0	Deleted reference to USEPA Method 3510C in Table 10, Element 13. Replaced with "Appendix 6" which contains a description of the actual methods used. Actual methods are a hybrid of protocols including USEPA Method 3510C.		
3/29/05	1.0	Removed field matrix spikes from Table 11, Element 14. No samples are spiked in the field, only in the lab.		
3/29/05	1.0	In Element 16 (GCMS instrument calibration) changed standards weight from 1000g to 500g.		
4/11/05	1.0	replaced Appendix 6 with revised version to reflect GCMS instrument calibration changes		

APPENDIX 1A

TMDL MONITORING PLAN SACRAMENTO RIVER BASIN 2005

TMDL Monitoring Plan
Sacramento River Basin
2005

Prepared by:

Michael L. Johnson
Henry J. Calanchini
Anja B. Wehrmann

October 12, 2004

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Introduction

In accordance with Clean Water Act Section 303(d), all states must identify "impaired" bodies of water and establish Total Maximum Daily Loads (TMDLs) for stressors that are the cause of the impairment. States must also develop monitoring and control plans for each stressor. In California, the State Water Resources Control Board and its nine subunits, the Regional Water Quality Control Boards (RWQCBs), are responsible for meeting section 303(d) requirements.

Numerous toxicity studies have found concentrations of the organophosphate pesticides diazinon and chlorpyrifos in Sacramento and San Joaquin waterways at levels that result in significant mortality or reproductive toxicity to the zooplankton species *Ceriodaphnia dubia* (Werner et al. 2000, Kuivila & Foe 1995). Since that time, several studies have been undertaken to further study the temporal and spatial occurrence of diazinon in the Sacramento River watershed, for the purposes of supporting TMDL development and observing any long-term changes in diazinon concentrations and loads in the Sacramento River watershed.

In 2003, the CVRWQCB approved Water Quality Objectives and a TMDL for diazinon in the Sacramento and Feather Rivers. The Water Quality Objectives set maximum allowable diazinon concentrations in the Sacramento and Feather Rivers, and the TMDL sets maximum allowable diazinon loads that can be discharged to the Sacramento River from five "subwatersheds": the Sacramento River Above Colusa, the Butte/Sutter Basin, the Colusa Basin, the Feather River and the Natomas Basin/American River.

This document describes the sampling plan to investigate the loads of diazinon and chlorpyrifos in the Sacramento River watershed associated with runoff events in January and February 2005.

OBJECTIVE

The primary objective of this sampling project is characterize the diazinon concentrations and loads in the lower Sacramento and Feather Rivers, and the concentrations and loads of diazinon being discharged to the Sacramento River from the following subwatersheds: the Sacramento River above Colusa, the Butte/Sutter Basin, the Colusa Basin Drain, and the Feather Rivers --during the 2004-2005 orchard dormant spray season. The objective will be achieved via the following tasks:

- Sampling six in the Sacramento River Basin-- Colusa Basin Drain near Knights Landing , Sacramento River at Colusa, Sacramento River at Tower Bridge, Sacramento River at Veterans Bridge, Feather River near Nicolaus/Verona and Sacramento Slough near Karnak for diazinon and other OP pesticides during two storm events in the 2004-2005 orchard dormant spray season.
- Using the concentrations found in the water collected for this study, and flow measurements taken calculate the loadings for diazinon in the sampled waterways

Sampling will be done in coordination with the California Department of Pesticide Regulation (DPR). DPR will monitor the Sacramento River at Colusa, Colusa Basin Drain, the Feather River near Verona, Natomas Cross Canal and the Sacramento River at Alamar (CDPR, 2005). Samples collected for this study and samples collected by DPR will be staggered to give the greatest temporal resolution at common sites.

Study Region and Sampling Locations

The Sacramento River Basin, in the north-central part of California, covers an area of about 70,000 km^2 (Kahrl 1979 cited in Dileanis et al. 2002) and delivers 31% of the state's runoff. Four major rivers feed this basin: the Sacramento River, the Feather River, the American River, and the Yuba River. The Sacramento Valley, an area of approximately 12,950 km^2 (Olmstead and Davis 1961 cited in Dileanis et al. 2002), is one of California's major agricultural regions. Within the valley there are about 5,957 km^2 of agricultural land of which approximately 751 km^2 is occupied by stone fruit and almond orchards (California Department of Water Resources 1990, 1994a, b, 1995a, b, c, d, 2000 cited in Dileanis et al. 2002). The main crops are rice, corn, wheat, sugar beets, alfalfa, orchard fruits, olives, tomatoes, and vegetables.

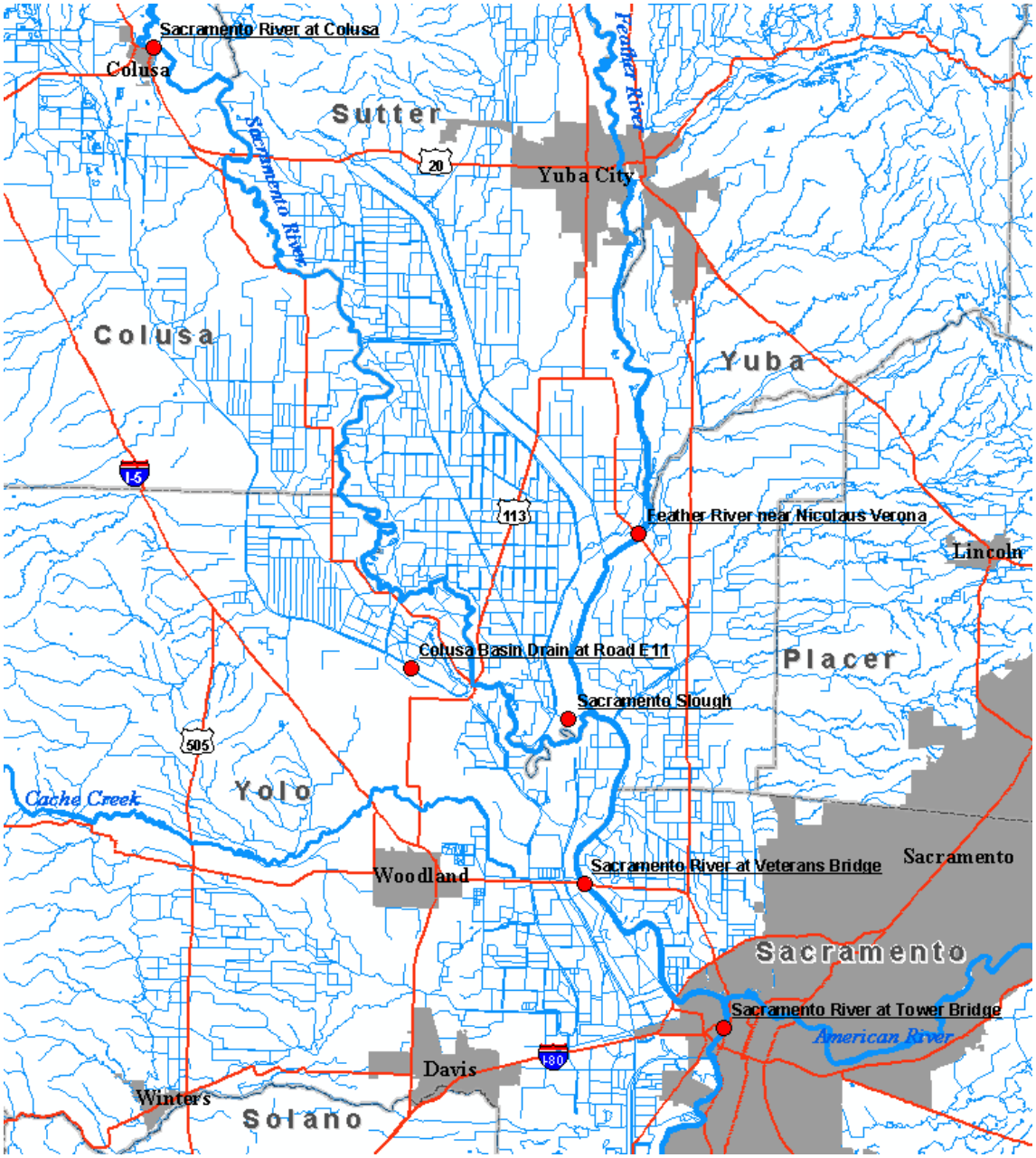
In the Sacramento River basin a total of six sites will be sampled between 14 and 16 times each during January and February 2004 (Table 1, Figure 1). The sites were selected to represent the possible sources of diazinon from agricultural and urban uses, and to characterization the spatial and temporal distribution of diazinon in the Sacramento River Basin. These include three sites on the mainstem of the Sacramento River (Figure 1c, Sacramento River at Colusa, Sacramento River at Sacramento, and Sacramento River at Veterans Bridge), one site on the Feather River near its outlet to the Sacramento River (Feather River near Nicolaus/Verona), one drainage canal that funnels runoff from thirty-two ephemeral

streams on the west side of the Sacramento Valley into the Sacramento River (Colusa Basin Drain), and one slough that bridges the Sutter Bypass with the Sacramento River (Sacramento Slough).

Table 1. 2004-05 Sacramento River Basin TMDL Pesticide Monitoring Sites

Site name	Site ID	Site Description	Latitude	Longitude
Colusa Basin Drain near Knights Landing	11390890	Collect integrated grab sample from bridge on Road E11 approximately 3.3 miles upstream of the confluence with the Sacramento River	38° 48' 44"	121° 46' 23"
Sacramento River at Colusa, CA	11389500	Collect integrated grab sample from bridge on River Road at Colusa	39° 12' 51"	121° 59' 57"
Sacramento River at Tower Bridge	383430121302001	Collect velocity weighted sample using D77 from boat on upstream side of Tower Bridge in downtown Sacramento	38° 34' 50"	121° 30' 26"
Sacramento River at Veterans Bridge	384027121373401	Collect velocity weighted sample using D77 from boat on upstream side of Veteran's Bridge near Alamar	38° 40' 31"	121° 37' 38"
Feather River near Nicolaus / Verona	384752121375301	Collect velocity weighted sample using D77 from boat approximately 7.5 miles upstream of Verona above confluence with Sutter Bypass	38° 53' 15"	121° 36' 35"
Sacramento Slough near Karnak	384649121381101	Collect velocity weighted sample using D77 from boat in Sacramento Slough near Karnak	38° 46' 49"	121° 38' 31"

Figure 1. The six sampling sites in the Sacramento River Basin to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05.



Personnel Resources

Sample collection will be performed by the Aquatic Ecosystems Analysis Laboratory (AEAL) of University of California, Davis under Contract No. 02-210-150 with the Central Valley Regional Water Quality Control Board. Sample analysis will be performed by the California Department of Food and Agriculture's (CDFA) Center for

Analytical Chemistry in Sacramento, CA. The primary project personnel include a contract manager, a technical reviewer from the CVRWQCB, a project manager and a project supervisor from UC Davis.

Jay Rowan (CVRWQCB) - Contract Manager: The contract manager is responsible for obtaining all services and analytical results/reports from the CDFA Analysis Lab contractor.

Dr. Michael Johnson (UCD) - Project manager: The project manager will work with all assigned Regional Board monitoring staff directly to provide guidance on sampling locations and timing of sample collection. The project manager will inform monitoring staff about sample collection and sample transport to California Department of Food and Agriculture Center for Analytical Chemistry (CDFA). The project manager will obtain a copy of the Chain of Custody (COC) after each sampling day from each sampling crew. The project manager will receive the chemical analysis results from CDFA Lab contract manager and prepare a monitoring program report including lab analysis results.

Daniel McClure (CVRWQCB) - Technical Reviewer: Technical Reviewer provides advice in determining the sampling sites, frequency, and time periods and the Technical Reviewer is responsible for overseeing budgetary expenses related to this monitoring study.

Henry Calanchini (AEAL) – Project Supervisor: The project supervisor will assist the project manager by hiring, training and supervising all monitoring staff and contributing to the monitoring program report. The project supervisor will be responsible for monitoring spray application and weather conditions and, in coordination with the technical reviewer, will determine when to begin sampling each storm event.

Sample Collection Period

The orchard dormant spray season in the Sacramento Valley generally begins in late December to early January and ends by late February to early March. Regional Board dormant spray monitoring will begin in January 2005 and continue through February 2005.

Two storm events will be sampled during the orchard dormant spray season at the six waterway sites; samples will be collected daily for up to eight consecutive days during each storm event. Sampling events

will begin when enough rainfall has fallen to cause runoff in the orchards where diazinon is applied as a dormant spray crop. (The general rule of thumb is that runoff will occur when at least 0.50 inches of rain has fallen inside 24 hours on the Sacramento Valley Floor, although it can take less or more runoff, depending on how saturated the soil is. Unless otherwise determined by the Project Manager and/or Technical Reviewer, this general rule of thumb will be used to determine when a sampling event begins.. For each storm event, samples will be collected and transported on the same day, when possible, to the CDFA lab for analysis.

Appendix A lists the six sampling sites, the number of samples scheduled for collection--including environmental samples and Quality Assurance/Quality Control (QA/QC) samples –and the sampling schedule. The project manager may adjust this schedule during the monitoring program as environmental factors dictate.

Sample Collection Procedures

Standard Operating Procedures for Collecting Water Samples in the Sacramento River Basin can be found in Appendix B.

Field Sheet

One field sheet will be completed at each monitoring site. Environmental and QC sample times will be recorded on the field sheet. Also recorded are the type(s) of QC collected (if any), the date, water quality parameters (temp, EC, pH), weather conditions, stream conditions, approximate location in the stream at which the sample was collected and any pertinent observations (inputs, dead fish, etc).

Discharge Measurements

Manual discharge measurements will be taken using a USGS Type AA current meter at Colusa Basin Drain. Discharge for the Sacramento River at Colusa will be obtained from the internet using the COL gage on the California Data Exchange Center (CDEC) website: http://cdec.water.ca.gov/ . Discharge at Sacramento River at Sacramento Slough and the Feather River near Verona will be measured at time of sample collection using a boat and an Acoustic Doppler Current Profiler (ADCP).

Sample Quality Control and Analysis

Field Quality Control Samples

During each monitoring season, additional samples will be collected for QA/QC. The frequency that matrix spike, duplicates, and field blanks are collected are based on the total number of environmental samples collected during this monitoring project. The number of QA/QC samples will amount to about 15 percent of the total number of environmental samples to be collected during this monitoring project. See Appendix A for the frequency and distribution of QC samples.

The QA/QC samples will include sample duplicates, equipment blanks, and matrix spikes. Sample duplicates are used to evaluate variability; equipment blanks to evaluate possible contamination during sample collection; and matrix spikes to evaluate recovery of constituents by the analytical techniques. The procedures for the QA/QC samples are based on the Sacramento, Delta and San Joaquin River Basins Organophosphorus Pesticides TMDL Quality Assurance Project Plan (Calanchini, 2004).

Laboratory Quality Control Samples

Laboratory quality control samples will be prepared at the laboratory. The procedures for laboratory quality control samples will be based on the Sacramento, Delta and San Joaquin River Basins TMDL Quality Assurance Project Plan.

Sample Documentation and Transfer to the Analytical Laboratory

A Regional Board chain of custody (COC) form will be completed for every sample. All samples will be transported to the California Department of Food and Agriculture (CDFA) Lab:

California Department of Food and Agriculture,
Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95832

Project Manager at CDFA Lab: Mark Lee
Contract No. 1-129-150

When delivering the samples, the original signed COC form is submitted to the CDFA Lab technician. A copy for Regional Board records is obtained prior to leaving the CDFA Lab. The copy includes both the

signature of the individual who relinquished the samples and the signature of the CDFA Lab technician that accepted the samples. If the CDFA lab is closed (if the sampling day exceeds their business hours or it is a holiday), samples are transported to UCD for storage until delivery the next day.

Chemical analysis and reporting

All samples will be analyzed for diazinon, chlorpyrifos, and other selected pesticides by the CDFA (Table 2). The CDFA conducts the chemical analysis using Gas Chromatography/Mass Spectrometry (GC/MS). The details of the method are described in Appendix C (CDFA 2003). The CDFA chemical analysis lab reports pertaining to this monitoring study will be sent by CDFA to the Project Manager for this monitoring study. The Project Manager will prepare a final monitoring report once all chemical analysis lab reports have been received and evaluated.

Table 2. List of analytes to be monitored during the 2004-05 dormant spray monitoring in the Sacramento River Basin.

Analyte	Limit of Detection (LOD) in ppb	Limit of Quantitation (LOQ) in ppb
Eptam (EPTC)	0.020	0.050
Simazine	0.005	0.200
Diazinon	0.007	0.020
Carbaryl	0.007	0.020
Metolachlor	0.007	0.020
Chlorpyrifos	0.004	0.010
Cyanazine	0.007	0.050
Dacthal (DCPA)	0.007	0.050
Methidathion	0.010	0.030
Propargite	0.150	0.500
Azinphos-methyl	0.007	0.050

Data management

The project manager will be responsible for data management, data analysis, and report preparation. The data includes chemical analysis results received from CDFA and all relevant field data and information collected by Regional Board staff.

Tasks and Timelines

A summary of the tasks to be completed and the estimated dates of completion are listed in Table 3.

Table 3. Tasks and Timelines

Tasks	Due date
Notify the contract manager of sampling personnel	November-December 2004
Draft monitoring schedule	November-December 2004
Project manager provides sampling protocol to the sampling personnel	December 2004-January 2005
Start of sampling period	January 2005
Chemical analysis report	Approximately four weeks after sending the samples to the lab
End of sampling period	May 2005
Monitoring report - draft	June 2005
Monitoring report - final	August 2005

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APPENDIX 1B

TMDL MONITORING PLAN SACRAMENTO - SAN JOAQUIN DELTA 2005

TMDL Monitoring Plan
Sacramento - San Joaquin Delta
2005

Prepared by:

Henry J. Calanchini
Anja B. Wehrmann
Michael L. Johnson

October 22, 2004

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Introduction

In accordance with Clean Water Act Section 303(d), all states must identify "impaired" bodies of water and establish Total Maximum Daily Loads (TMDLs) for stressors that are the cause of the impairment. States must also develop monitoring and control plans for each stressor. In California, the State Water Resources Control Board and its nine subunits, the Regional Water Quality Control Boards (RWQCBs), are responsible for meeting section 303(d) requirements.

Preliminary surveys of California's urban waterways (Bailey et al. 2000) detected high concentrations of the organophosphate pesticides (OPs) diazinon and chlorpyrifos, chemicals used to control domestic and agricultural pests. Research has linked OPs to biochemical, immunological, physiological, behavioral, and hormonal effects in wildlife species (Sheffield & Lochmiller 2001, Beauvais et al. 2000, Boone et al. 2001, Carey et al. 1999). Numerous toxicity studies have found OP concentrations in Sacramento and San Joaquin waterways at levels that result in significant mortality or reproductive toxicity to the zooplankton species *Ceriodaphnia dubia* (Werner et al. 2000, Kuivila & Foe 1995). In 1998, California placed the Delta waterways on the 303(d) list of impaired bodies for diazinon and chlorpyrifos, and instituted a monitoring plan.

The first monitoring study to support diazinon and chlorpyrifos TMDL development for the Central Valley Regional Water Quality Control Board (CVRWQCB) was conducted by the California Department of Pesticide Regulation and the U.S. Geological Survey (USGS) during winter (dormant season) 2000 (Dileanis et al. 2002). The CVRWQCB and the USGS continued monitoring in 2001 and 2002 (D. Beaulaurier, personal communication, April 2003).

In 2002, California updated its 303(d) list (see http://www.swrcb.ca.gov/303dupdate.html). Diazinon and chlorpyrifos were still ranked as high priority substances responsible for impairing water quality in many Delta waterways. Although numerous studies have examined the occurrence of diazinon and chlorpyrifos in Central Valley waterways, the CVRWQCB determined that additional data was required to finalize the TMDLs.

A study was undertaken to provide those data to the CVRWQCB. This document describes the sampling plan to investigate the loads of diazinon and chlorpyrifos in the Sacramento-San Joaquin Delta waterways associated with runoff events occurring between January and March 2005.

Objective

The primary objective of this sampling project is to monitor seven diazinon and/or chlorpyrifos-impaired sites in the Sacramento-San Joaquin Delta waterway during the 2004-2005 orchard dormant spray season, and post-orchard dormant spray season, to further characterize and define the sources of diazinon and chlorpyrifos insecticides that cause surface water contamination and toxic conditions to aquatic life. The study focuses on measuring and assessing diazinon and chlorpyrifos concentrations and loads in waterways during and following the orchard dormant spray season. The objective will be achieved via the following tasks:

- Sample seven Sacramento-San Joaquin Delta monitoring sites for diazinon and chlorpyrifos for two storm events during the 2004-2005 orchard dormant spray season, and on a weekly basis following the dormant spray season, to measure the concentrations of diazinon and chlorpyrifos in collected surface water samples.
- Using the concentrations found in the water collected for this study, calculate the loadings for diazinon and chlorpyrifos in the sampled waterways for which discharge estimates are available.

Study Region and Sampling Locations

The Sacramento-San Joaquin Delta contains over 2,024 km^2 of irrigated farmland (Saleh et al. 2003). As part of the California water delivery system, water exported from the Delta is delivered to millions of hectares of farmland south of the Delta and provides municipal water to two-thirds of the population of California (Templin and Cherry 1997). The Delta receives 84% of its fresh water from the Sacramento River, 13% from the San Joaquin River, and the remaining 3% from the Cosumnes River, the Mokelumne River, and several other smaller rivers (Jassby and Cloern 2000).

In the Sacramento-San Joaquin Delta a total of seven sites will be sampled in two storm events during January and February 2005 (Table 1, Figure 1). The sites were selected to represent the possible sources of diazinon and chlorpyrifos from agricultural and urban uses, and to characterization the spatial and temporal distribution of diazinon and chlorpyrifos in the Sacramento-San Joaquin Delta area.

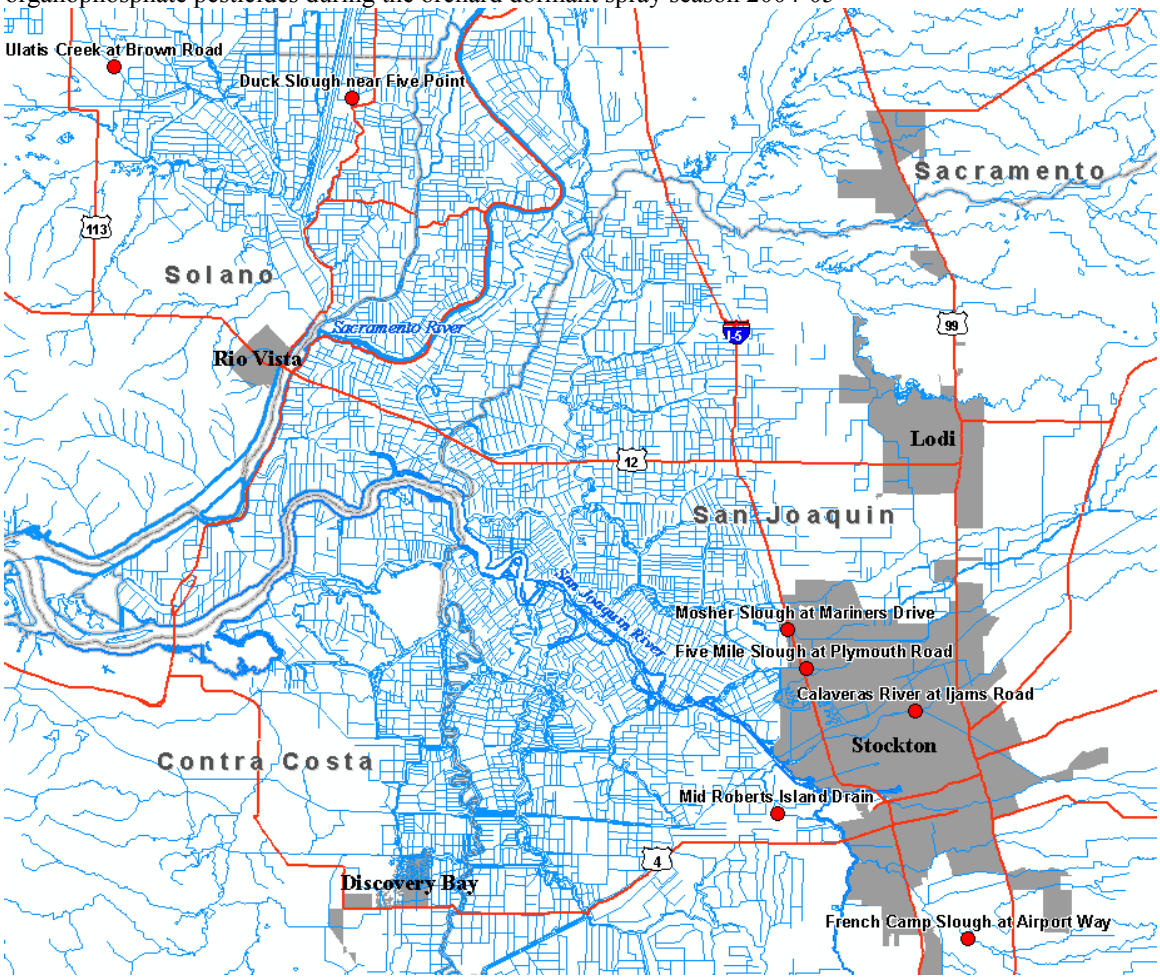
These sites include one on the mainstem of the Calaveras River (Calaveras River at Ijams Road), two Sacramento River tributaries (Ulatis Creek at Brown Road and Duck Slough at Five Points Marina),

one irrigation pump from Burns cutoff which is a tributary to the San Joaquin River—(Mid Roberts Island Drain), and three tributaries to the San Joaquin River (Mosher Slough at Mariners Drive, French Camp Slough at Airport Way and Five Mile Slough at Plymouth Road).

Table 1. 2004-05 Sacramento-San Joaquin Delta TMDL Pesticide Monitoring Sites

Site ID	Site Name	Site description	Latitude	Longitude
Delt02	Mosher Slough at Mariners Drive	Bridge at Mariners Dr.	38º 1' 58"	121º 21' 50"
Delt03	Five Mile Slough at Plymouth	West side of Plymouth Dr. (five culverts, southwest corner of golf course)	38º 0' 50"	121º 21' 6"
Delt04	Calaveras River at Ijams Rd	The bridge off Ijams Rd. (during dry season, samples may be taken from the under bridge because the river is very shallow and the bridge is high).	37º 59' 36"	121º 17' 0"
Delt05	Mid Roberts Island Drain	South Woodsbro Road before discharge pump where the drain goes to Burns Cutoff.	37º 56' 35"	121º 22' 9"
Delt06	French Camp Slough at Airport Way		37°52’ 00”	121° 14’ 01”
Delt10	Ulatis creek at Brown Rd	Under bridge at Brown Rd.	38º 18' 26"	121º 47' 34"
Delt11	Duck Slough	Middle of drain at discharge pump platform.	38º 17' 36"	121º 38' 39"

Fig. 1 The seven sampling sites in the Sacramento-San Joaquin Delta to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05



Personnel Resources

Sample collection will be performed by the Aquatic Ecosystems Analysis Laboratory (AEAL) of University of California, Davis under Contract No. 02-210-150 with the Central Valley Regional Water Quality Control Board. Sample analysis will be performed by the California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry in Sacramento, CA. The primary project personnel include a contract manager, a technical reviewer from the CVRWQCB, a project manager and a project supervisor from UC Davis.

Jay Rowan (CVRWQCB) - Contract Manager: The contract manager is responsible for obtaining all services and analytical results/reports from the CDFA Analysis Lab contractor.

Dr. Michael Johnson (AEAL) - Project Manager: The project manager will work with all assigned Regional Board monitoring staff directly to provide guidance on sampling locations and timing of sample collection. The project manager will inform monitoring staff about sample collection and sample transport to California Department of Food and Agriculture Center for Analytical Chemistry. The project manager will obtain a copy of the Chain of Custody (COC) after each sampling day from each sampling crew. The project manager will receive the chemical analysis results from CDFA Lab contract manager and prepare a monitoring program report including lab analysis results.

Jamie Lu (CVRWQCB) -Technical Reviewer: Technical Reviewer provides advice in determining the sampling sites, frequency, and time periods and the Technical Reviewer is responsible for overseeing budgetary expenses related to this monitoring study.

Henry Calanchini (AEAL) – Project Supervisor: The project supervisor will assist the project manager by hiring, training and supervising all monitoring staff and contributing to the monitoring program report. The project supervisor will be responsible for monitoring spray application and weather conditions and, in coordination with the technical reviewer, will determine when to begin sampling each storm event. The project supervisor will fax copies of COC's and field sheets to the technical reviewer on a daily basis as they are generated.

Sampling Site Descriptions

The seven sampling sites in the Sacramento-San Joaquin Delta are:

Mosher Slough at Mariners Drive: Sample will be taken from the south bank of the slough at Mariners Dr.

Five-Mile Slough at Plymouth Road: Sample will be taken from the west side of Plymouth Dr. where five culverts merge.

Calaveras River at Ijams Road: Sample will be taken from under the bridge at Ijams Rd.

Mid Roberts Island Drain: Sample will be taken from South Woodsbro Road before the discharge pump, where the drain goes to Burns Cutoff.

French Camp Slough at Airport Way:

Ulatis Creek at Brown Road: Sample will be taken from under the bridge on Brown Rd.

Duck Slough: Sample will be taken from the middle of the drain discharge pump platform at Five Points Marina.

Sample Collection Period

The orchard dormant spray season in the Sacramento-San Joaquin Delta area generally begins in early to mid-January and ends by late February to early March. Dormant spray season waterway monitoring will begin in January and continue through February; post-dormant spray season waterway monitoring will begin approximately in early March and continue through May 2005, weather permitting.

A total of two storm events will be sampled during the orchard dormant spray season. Sampling will occur for five consecutive days during each storm event. Post-orchard dormant spray season, weekly non-event samples will be taken at the seven waterway sites. Sampling events will begin when at least 0.25 inches of rain has fallen inside 24 hours within the Sacramento-San Joaquin Delta area, unless otherwise determined by the Project Manager and/or Technical Reviewer. For each storm event, samples will be collected and transported on the same day, when possible, to the CDFA lab for analysis.

Appendix A lists the seven sampling sites, the number of samples scheduled for collection--including environmental samples and Quality Assurance/Quality Control (QA/QC) samples –and the sampling schedule. The project manager may adjust this schedule during the monitoring program due to environmental factors.

Sample Collection Procedures

Standard Operating Procedures for Collecting Water Samples in the Sacramento-San Joaquin Delta are found in Appendix B.

Field Sheet

One field sheet will be completed at each monitoring site. Environmental and QC sample times will be recorded on the field sheet. Also recorded are the type(s) of QC collected (if any), the date, water quality

parameters (temp, EC, pH), weather conditions, stream conditions, approximate location in the stream at which the sample was collected and any pertinent observations (inputs, dead fish, etc).

Flow Measurements

Manual flow measurements will be taken at Ulatis Creek at Brown Road and the Calaveras River at Ijams Road using a Swoffer Model 2100 current meter. The remaining sites will not have flow measurements taken because the waterways are either too large to make discharge measurements practical or they are complicated by tidal influence. Pumping station records will be documented on the field sheets. Pumping records will be documented for Mid-Roberts Island Drain and Duck Slough. In addition, precipitation data will be documented for Thornton, Brentwood, and Dixon, California. Also storm patterns and rainfall data will be documented as accurately as possible to create a detailed record of the event.

Sample Quality Control and Analysis

Field Quality Control Samples

During each monitoring season, additional samples will be collected for QA/QC. The frequency for collection of matrix spike, duplicates, and field blanks is based on the total number of environmental samples collected during this monitoring project. The number of QA/QC samples will amount to about 15 percent of the total number of environmental samples to be collected during this monitoring project. See Appendix A for the frequency and distribution of QC samples.

The QA/QC samples will include sample duplicates, equipment blanks, and matrix spikes. The procedures for the QA/QC samples are based on the San Joaquin River TMDL Quality Assurance Project Plan (Azimi and Reyes 2002).

Laboratory Quality Control Samples

Laboratory quality control samples will be prepared at the laboratory. The procedures for laboratory quality control samples will be based on the San Joaquin River TMDL Quality Assurance Project Plan (Azimi and Reyes 2002).

Sample Documentation and Transfer to the Analytical Laboratory

A Regional Board chain of custody (COC) form will be completed for every sample. All samples will be transported to the California Department of Food and Agriculture (CDFA) Lab:

California Department of Food and Agriculture,
Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95832

Project Manager at CDFA Lab: Mark Lee
Contract No. 1-129-150

When delivering the samples, the original signed COC form is submitted to the CDFA Lab technician. A copy for Regional Board records is obtained prior to leaving the CDFA Lab. The copy includes both the signature of the individual who relinquished the samples and the signature of the CDFA Lab technician that accepted the samples. If the CDFA lab is closed (if the sampling day exceeds their business hours or it is a holiday), samples are transported to UCD for storage until delivery the next day.

Chemical analysis and reporting

All samples will be analyzed for diazinon, chlorpyrifos, and other selected pesticides by the CDFA (Table 2). The CDFA conducts the chemical analysis using Gas Chromatography/Mass Spectrometry (GC/MS). The details of the method are described in Appendix C (CDFA 2003). The relevant CDFA chemical analysis lab reports pertaining to this monitoring study will be sent by CDFA to the Project Manager for this monitoring study. The Project Manager will prepare a final monitoring report once all chemical analysis lab reports have been received and evaluated.

Table 2. List of analytes to be monitored during the 2004-05 dormant spray monitoring in the Sacramento-San Joaquin Delta.

Analyte	Limit of Detection (LOD) in ppb	Limit of Quantitation (LOQ) in ppb
Eptam (EPTC)	0.020	0.050
Simazine	0.005	0.200
Diazinon	0.007	0.020
Carbaryl	0.007	0.020
Metolachlor	0.007	0.020
Chlorpyrifos	0.004	0.010
Cyanazine	0.007	0.050
Dacthal (DCPA)	0.007	0.050
Methidathion	0.010	0.030
Propargite	0.150	0.500
Azinphos-methyl	0.007	0.050

Data management

The project manager will be responsible for data management, data analysis, and report preparation. The data includes chemical analysis results received from CDFA and all relevant field data and information collected by Regional Board staff.

Tasks and Timelines

A summary of the tasks to be completed and the estimated dates of completion are listed in Table 3.

Table 3. **Tasks and Timelines**

Tasks	Due date
Notify the contract manager of sampling personnel	November-December 2004
Draft monitoring schedule	November-December 2004
Project manager provides sampling protocol to the sampling personnel	December 2004-January 2005
Start of sampling period	January 2005
Chemical analysis report	Approximately four weeks after sending the samples to the lab
End of sampling period	May 2005
Monitoring report - draft	June 2005
Monitoring report - final	August 2005

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APPENDIX 1C

TMDL MONITORING PLAN SAN JOAQUIN RIVER BASIN 2005

TMDL Monitoring Plan

San Joaquin River Basin

2005

Prepared by:

Henry J. Calanchini
Anja B. Wehrmann
Michael L. Johnson

Updated 16 December 2004

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Introduction

In accordance with Clean Water Act Section 303(d), all states must identify "impaired" bodies of water and establish Total Maximum Daily Loads (TMDLs) for stressors that are the cause of the impairment. States must also develop monitoring and control plans for each stressor. In California, the State Water Resources Control Board and its nine Regional Water Quality Control Boards (RWQCBs), are responsible for meeting section 303(d) requirements.

Preliminary surveys of California's urban waterways (Bailey et al. 2000) detected high concentrations of the organophosphate pesticides (OPs) diazinon and chlorpyrifos, used to control domestic and agricultural pests. Research has linked OPs to biochemical, immunological, physiological, behavioral, and hormonal effects in wildlife species (Sheffield & Lochmiller 2001, Beauvais et al. 2000, Boone et al. 2001, Carey et al. 1999). Numerous toxicity studies have found OP concentrations in Sacramento and San Joaquin waterways at levels that result in significant mortality or reproductive toxicity to the zooplankton species *Ceriodaphnia dubia* (Werner et al. 2000, Kuivila & Foe 1995). In 1998, California placed the San Joaquin River on the 303(d) list of impaired bodies for diazinon and chlorpyrifos, and instituted a monitoring plan.

The first monitoring study to support diazinon and chlorpyrifos TMDL development for the Central Valley Regional Water Quality Control Board (CVRWQCB) was conducted by the California Department of Pesticide Regulation and the U.S. Geological Survey (USGS) during winter (dormant season) 2000 (Dileanis et al. 2002). The CVRWQCB and the USGS continued monitoring in 2001 and 2002 (D. Beaulaurier, personal communication, April 2003).

In 2002, California updated its 303(d) list (see http://www.swrcb.ca.gov/303dupdate.html). Diazinon and chlorpyrifos were still ranked as high priority substances responsible for impairing water quality in the San Joaquin River. Although numerous studies have examined the occurrence of diazinon and chlorpyrifos in Central Valley waterways, the CVRWQCB determined that additional data was required to finalize the TMDLs.

A study was undertaken to provide those data to the CVRWQCB. This document describes the sampling plan to investigate the loads of diazinon and chlorpyrifos in the Sacramento and -San Joaquin Rivers and Delta waterways associated with runoff events occurring between December 2004and August 2005.

Objective

The primary objective of this sampling project is to monitor six select diazinon and/or chlorpyrifos-impaired sites in the San Joaquin River Basin--San Joaquin River at Vernalis, San Joaquin River at Lander Avenue, San Joaquin River at Patterson, Stanislaus River at Caswell State Park, Tuolumne River at Shiloh Road, and Merced River at River Road--during the orchard dormant spray season (December 2004- Feb 2005) and the irrigation season (March 2005-August 2005) to further characterize and define the sources of diazinon and chlorpyrifos insecticides that cause surface water contamination and toxic conditions to aquatic life. The study focuses on monitoring and assessing diazinon and chlorpyrifos concentrations and loads in waterways. The objective will be achieved via the following tasks:

- Sample six San Joaquin River Basin monitoring sites for diazinon and chlorpyrifos for three storm events during the 2004-2005 orchard dormant spray season to measure the concentrations of diazinon and chlorpyrifos in collected surface water samples.
- Sample five San Joaquin River Basin monitoring sites for diazinon and chlorpyrifos weekly for 3 or 4 selected months during the irrigation season (March- August 2005) to measure the concentrations of diazinon and chlorpyrifos in collected surface water samples.
- Using the concentrations found in the water collected for this study, calculate the loadings for diazinon and chlorpyrifos in the sampled waterways and track potential changes in diazinon and chlorpyrifos concentrations and loads in San Joaquin River Basin waterways.

Study Region and Sampling Locations

The San Joaquin Basin can be divided into two parts: the northern section, drained by the San Joaquin River and its tributaries, and the Tulare Basin in the far southern part of the Central Valley. The San Joaquin-Tulare basin is approximately 80,808 km^2 (Panshin et al. 1998) and drains about 9% of California's runoff. The San Joaquin study sites in this report are contained entirely within the perennial basin of the San Joaquin River drainage of approximately 19,024 km^2 (Saleh et al. 2003). The major sources of water feeding the perennial San Joaquin Basin

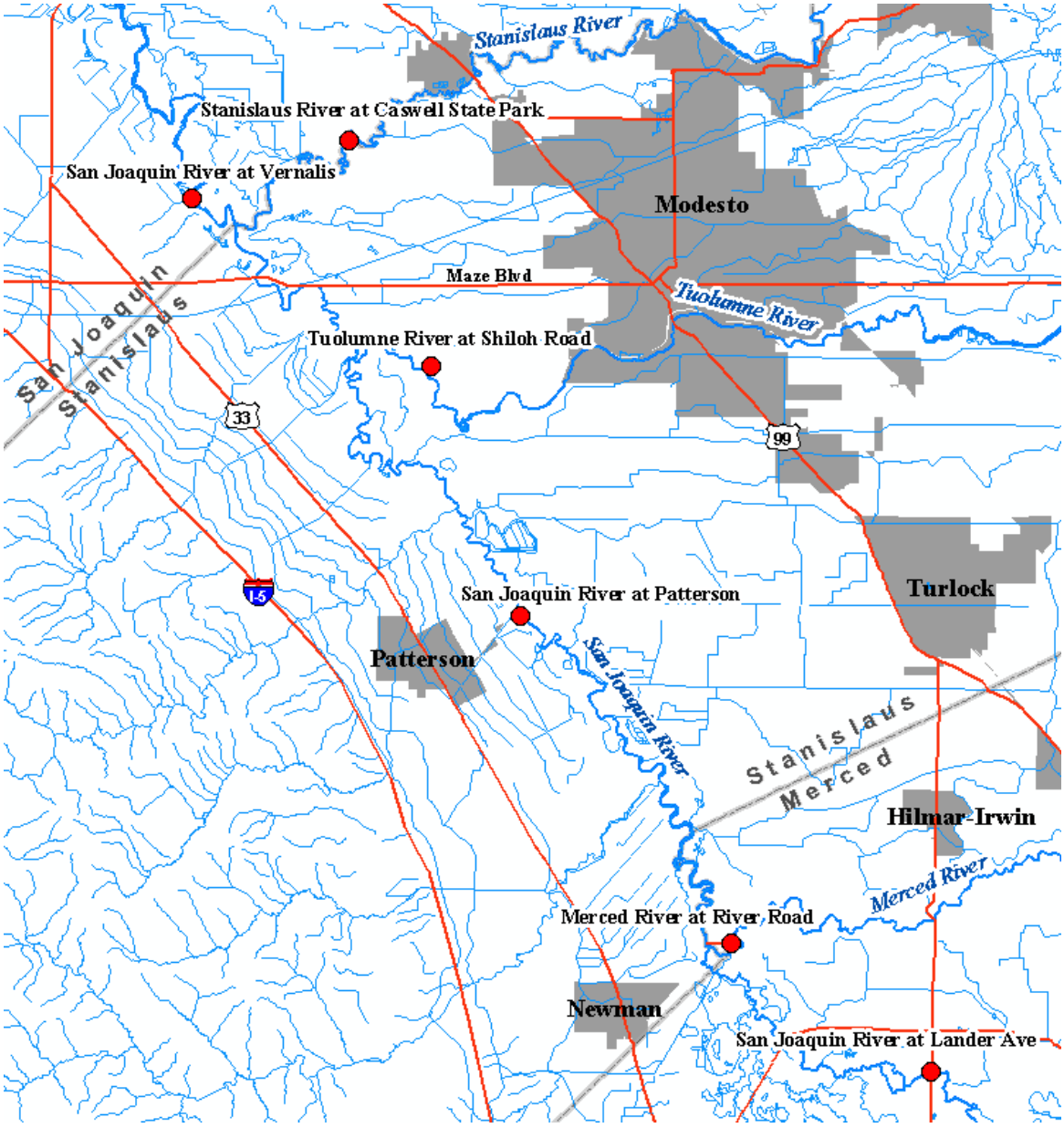
are the Merced River, the Tuolumne River, the Stanislaus River and the San Joaquin River. Crops produced in the region include cotton, corn, grains, grapes, vegetables, orchard fruits, nuts, citrus, and alfalfa. There are about 6,088 km^2 of agricultural land in the perennial San Joaquin Basin (Saleh et al. 2003).

In the San Joaquin basin a total of six sites will be sampled between 4 and 24 times each between December and February2005 (dormant season) and between March and August 2005 (irrigation season) (Table 1, Figure 1). The sites were selected to represent the possible sources of diazinon and chlorpyrifos from agricultural and urban uses, and to characterization the spatial and temporal distribution of diazinon and chlorpyrifos in the San Joaquin Basin. These sites include three on the mainstem of the San Joaquin River (Lander Avenue, Patterson and Vernalis), and basin outlet sites on the three major east-side tributaries (Merced River at River Road, Tuolumne River at Shilo Road, and Stanislaus River at Caswell State Park). For a description of each site see Table 1.

Table 1. 2004-05 San Joaquin River Basin TMDL Pesticide Monitoring Sites

Site ID	Site Name	Site description	Latitude	Longitude
11273500	Merced River at River Road	Sample collected from upstream side of historic bridge near Hatfield Park	37°21'04"	120°57'39"
11290200	Tuolumne River at Shiloh Road	Sample collected from upstream side of Shilo Road bridge	37°36'12"	121°07'49"
11303500	San Joaquin River at Vernalis	Sample collected from the upstream side of the bridge on Airport Way	37°40'34"	121°15'51"
374209121103800	Stanislaus River at Caswell State Park	Sample collected in Caswell Memorial State Park from river bank behind campsite #24	37°42'09"	121°10'38"
11260815	San Joaquin River at Lander Avenue	Sample collected from the east side of the Lander Avenue Bridge	37º 17’ 43’	120º 51’01’
11274570	San Joaquin River at Patterson	Sample collected from boat launch ramp on Old Las Palmas Avenue	37º 29’ 52’	121º 04’ 54’

Figure 1. The six sampling sites in the San Joaquin Basin to be monitored for organophosphate pesticides during the orchard dormant spray season 2004-05.



Personnel Resources

Sample collection will be performed by Post Graduate Researchers working for the Regional Board under contract with UC Davis. Sample analysis will be performed by the California Department of Food and Agriculture's (CDFA) Center for Analytical Chemistry in Sacramento, CA. The primary project personnel include two

post-graduate researchers, a contract manager, a technical reviewer from the CVRWQCB, a project manager and a project supervisor from UC Davis.

Jay Rowan (CVRWQCB) - Contract Manager: The contract manager is responsible for obtaining all services and analytical results/reports from the CDFA Analysis Lab contractor., in coordination with the technical manager.

Dr. Michael Johnson (UCD) - Project manager: The project manager will work with all assigned Regional Board monitoring staff directly to provide guidance on sampling locations and timing of sample collection. The project manager will inform monitoring staff about sample collection and sample transport to California Department of Food and Agriculture Center for Analytical Chemistry (CDFA). The project manager will obtain a copy of the Chain of Custody (COC) after each sampling day from each sampling crew. The project manager will receive the chemical analysis results from CDFA Lab contract manager and prepare a monitoring program report including lab analysis results.

Diane Beaulaurier (CVRWQCB) - Technical Reviewer: Technical Reviewer provides advice in determining the sampling sites, frequency, and time periods and the Technical Reviewer is responsible for overseeing budgetary expenses related to this monitoring study.

Henry Calanchini (AEAL) – Project Supervisor: The project supervisor will assist the project manager by hiring, training and supervising all monitoring staff and contributing to the monitoring program report. The project supervisor will be responsible for monitoring spray application and weather conditions and, in coordination with the technical reviewer, will determine when to begin sampling each storm event. The project supervisor will fax copies of COC's and field sheets to the technical reviewer on a daily basis as they are generated.

Sample Collection Period

The orchard dormant spray season in the San Joaquin Valley generally begins in late December to early January and ends by late February to early March. Dormant spray monitoring will begin in January 2005 and continue through February 2005.

Three storm events will be sampled during the orchard dormant spray season at the six waterway sites; samples will be collected daily for up to eight consecutive days during each storm event. Sampling events will begin when at least 0.50 inches of rain has fallen inside 24 hours within the San Joaquin Basin, unless otherwise determined by the Project Manager and/or Technical Reviewer. For each storm event samples will be collected and transported on the same day, when possible, to the CDFA lab for analysis.

Appendix A lists the six sampling sites, the number of samples scheduled for collection--including environmental samples and Quality Assurance/Quality Control (QA/QC) samples –and the sampling schedule. The project manager may adjust this schedule during the monitoring program as environmental factors dictate.

The irrigation season begins in March and continues through August. Samples will be collected on a once weekly basis for selected months during this time period. It is currently estimated that samples will be collected weekly during March, April, July and August. Samples will be collected at the same locations where dormant samples are collected, and all other conditions will remain the same (i.e. transport to lab, etc.).

Sample Collection Procedures

Standard Operating Procedures for Collecting Water Samples in the San Joaquin River Basin are found in Appendix B.

Field Sheet

One field sheet will be completed at each monitoring site. Environmental and QC sample times will be recorded on the field sheet. Also recorded are the type(s) of QC collected (if any), the date, water quality parameters (temp, EC, pH), weather conditions, stream conditions, approximate location in the stream at which the sample was collected and any pertinent observations (inputs, dead fish, etc).

Flow Measurements

Manual flow measurements will not be taken at any of the San Joaquin River Basin monitoring sites for the following reasons:

San Joaquin River at Vernalis, Lander and Patterson: There are USGS gauging stations close to these sampling sites.

Stanislaus River at Caswell Park, Tuolumne River at Shiloh Road, and Merced River at River Road: The waterways are too large, and unsafe, to manually gage discharge without the use of a boat. Instead, discharge will be estimated by using data from existing USGS gages on each stream and adjusting for distance and time between the sampling sites and the nearest gages.

Sample Quality Control and Analysis

Field Quality Control Samples

During each monitoring season, additional samples will be collected for QA/QC. The frequency for collecting matrix spike, duplicates, and field blanks is based on the total number of environmental samples collected during this monitoring project. The number of QA/QC samples will amount to about 15 percent of the total number of environmental samples to be collected during this monitoring project. See Appendix A for the frequency and distribution of QC samples.

The QA/QC samples will include sample duplicates, equipment blanks, and matrix spikes. The procedures for the QA/QC samples are based on the San Joaquin River TMDL Quality Assurance Project Plan (Azimi and Reyes 2002).

Laboratory Quality Control Samples

Laboratory quality control samples will be prepared at the laboratory. The procedures for laboratory quality control samples will be based on the San Joaquin River TMDL Quality Assurance Project Plan (Azimi and Reyes 2002).

Sample Documentation and Transfer to the Analytical Laboratory

A Regional Board chain of custody (COC) form will be completed for every sample. All samples will be transported to the California Department of Food and Agriculture (CDFA) Lab:

California Department of Food and Agriculture,
Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, CA 95832

Project Manager at CDFA Lab: Mark Lee
Contract No. 1-129-150

When delivering the samples, the original signed COC form is submitted to the CDFA Lab technician. A copy for Regional Board records is obtained prior to leaving the CDFA Lab. The copy includes both the signature of the individual who relinquished the samples and the signature of the CDFA Lab technician that accepted the samples. If the CDFA lab is closed (if the sampling day exceeds their business hours or it is a holiday), samples are transported to UCD for storage until delivery the next day.

Chemical analysis and reporting

All samples will be analyzed for diazinon, chlorpyrifos, and other selected pesticides by the CDFA (Table 2). The CDFA conducts the chemical analysis using Gas Chromatography/Mass Spectrometry (GC/MS). The details of the method are described in Appendix C (CDFA 2003). The relevant CDFA chemical analysis lab reports pertaining to this monitoring study will be sent by CDFA to the Project Manager and the Technical Manager for this monitoring study. The Project Manager will prepare a final monitoring report once all chemical analysis lab reports have been received and evaluated.

Table 2. List of analytes to be monitored during the 2004-05 dormant spray monitoring in the San Joaquin River Basin.

Analyte	Limit of Detection (LOD) in ppb	Limit of Quantitation (LOQ) in ppb
Eptam (EPTC)	0.020	0.050
Simazine	0.005	0.200
Diazinon	0.007	0.020
Carbaryl	0.007	0.020
Metolachlor	0.007	0.020
Chlorpyrifos	0.004	0.010
Cyanazine	0.007	0.050
Dacthal (DCPA)	0.007	0.050
Methidathion	0.010	0.030
Propargite	0.150	0.500
Azinphos-methyl	0.007	0.050

Data management

The project manager will be responsible for data management, data analysis, and report preparation. The data includes chemical analysis results received from CDFA and all relevant field data and information collected by Regional Board staff.

Tasks and Timelines

A summary of the tasks to be completed and the estimated dates of completion are listed in Table 3.

Table 3. Tasks and Timelines

Tasks	Due date
Notify the contract manager of sampling personnel	November-December 2004
Draft monitoring schedule	November-December 2004
Project manager provides sampling protocol to the sampling personnel	December 2004-January 2005
Start of sampling period	January 2005
Chemical analysis report	Approximately four weeks after sending the samples to the lab
End of sampling period	August 2005
Dormant season Monitoring report - draft	June 2005
Dormant season Monitoring report - final	August 2005
Irrigation season monitoring report - draft	November 2005
Irrigation season monitoring report - final	January 2006

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APPENDIX 2A

SCHEDULE OF PRIMARY AND QUALITY CONTROL SAMPLES FOR 2004-05
SACRAMENTO RIVER BASIN
TMDL MONITORING

Appendix 2a. Schedule of Primary and Quality Control Samples for 2004-05 Sacramento River Basin TMDL Monitoring

Sample Site		Sacramento R. at Colusa				Sacramento R at Tower Bridge				Colusa Basin Drain				Sacramento River at Veterans Bridge				Feather River near Nicolaus / Verona				Sacramento Slough			
Month	Week	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB
Jan	Storm day1	1	1			1				1				1				1				1			
	Storm day2	1				1		SEC		1				1				1				1		SEC	
	Storm day3	1				1				1			1	1				1				1			
	Storm Day4	1				1				1				1	1			1	1			1			
	Storm Day5	1				1				1				1				1		SPR		1			
	Storm Day6	1				1				1				1				1				1			1
	Storm Day7	1				1				1				1				1				1			
	Storm Day8					1								1								1			
Feb	Storm day1	1		SPR		1				1				1				1				1			
	Storm day2	1				1			1	1				1				1				1			
	Storm day3	1				1				1	1			1				1				1			
	Storm Day4	1				1				1				1		SPR		1				1			
	Storm Day5	1				1				1				1				1			1	1			
	Storm Day6	1			1	1				1				1				1				1	1		
	Storm Day7	1				1				1		SEC		1				1				1			
	Storm Day8					1								1								1			
Totals		14	1	1	1	16		1	1	14	1	1	1	16	1	1		14	1	1	1	16	1	1	1

OP= primary samples	**90**
SP = Matrix spike	5
EB = Environmental blank	5
FD = Field duplicate	6
Total QC's	**16**
Total Samples	**106**

Field duplicates are either
SPR = Split replicate
SEC = Sequential replicate

APPENDIX 2B

SCHEDULE OF PRIMARY AND QUALITY CONTROL SAMPLES FOR 2004-05 DELTA TMDL MONITORING

Appendix 2b. Schedule of Primary and Quality Control Samples for 2004-05 Delta TMDL Monitoring.

Month		Mosher Slough@ Mariners				Fivemile Slough @ Plymouth				Calaveras River @ Ijams				Mid-Robert IS D @ Woodbro				French Camp Slough @ Airport				Ulatis Creek @ Brown Rd				Duck Sl near FivePoint			
		Delt02				Delt03				Delt04				Delt05				Delt06				Delt10				Delt11			
Jan	Week	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB	OP	SP	FD	EB
	Storm day1	1		1		1				1				1				1				1	1			1			
	Storm day2	1				1			1	1				1				1				1				1		1	
	Storm day3	1				1				1	1			1				1				1				1			
	Storm Day4	1				1				1				1		1		1				1				1			
	Storm Day5	1				1				1				1				1			1	1				1			
Feb	Storm day1	1	1			1				1				1				1				1				1			
	Storm day2	1				1		1		1				1				1				1				1			
	Storm day3	1				1				1			1	1				1				1				1			
	Storm Day4	1				1				1				1	1			1				1			1	1			
	Storm Day5	1				1				1				1				1		1		1				1	1		
Mar	Week1	1				1	1			1				1				1				1				1			
Mar	Week2	1				1				1		1		1				1				1				1			
Mar	Week3	1				1				1				1			1	1				1				1			
Mar	Week4	1				1				1				1				1				1		1		1			
Apr	Week1													1				1	1			1				1			
Apr	Week2													1				1				1				1			
Apr	Week3													1				1				1				1			1
Apr	Week4													1				1				1				1			
May	Week1													1				1				1	1			1			
May	Week2													1				1				1				1			
May	Week3													1		1		1				1				1			
May	Week4													1				1				1				1			
		14				14				14				22				22				22				22			
	QA's		1	1			1	1	1		1	1	1		1	2	1		1	1	1		2	1	1		1	1	1

SP = Matrix spike 130 Primary sample

FD = Field duplicate 22 QC sample

EB = Environmental blank 152 Total sample

APPENDIX 2C

SCHEDULE OF PRIMARY AND QUALITY CONTROL SAMPLES FOR 2004-05
SAN JOAQUIN RIVER BASIN
TMDL MONITORING

Appendix 2c. Schedule of Primary and Quality Control Samples for 2004-05 San Joaquin River Basin TMDL Monitoring

	Storm 1				**Storm 2**				**Storm 3**			
Site Name	Day1	Day 2	Day 3	Day 4	Day1	Day 2	Day 3	Day 4	Day1	Day 2	Day 3	Day 4
San Joaquin at Vernalis												
Environmental Sample	2	2	2	2	2	2	2	2	2	2	2	2
QC (S, D, B)	S 1				D 2				B 1			
Stanislaus River at CSP												
Environmental Sample	2	2	2	2	2	2	2	2	2	2	2	2
QC (S, D, B)		D 2				B 1				S 2		
Tuolumne River at Shilo Rd												
Environmental Sample	2	2	2	2	2	2	2	2	2	2	2	2
QC (S, D, B)			B 1				S 2				D 1	
SJR @ Lander Avenue												
Environmental Sample	1	1	1	1								
QC (S, D, B)	D											
SJR @ Patterson												
Environmental Sample					1	1	1	1	1	1	1	1
QC (S, D, B)								S			D	
Merced River at River Rd												
Environmental Sample	1	1	1	1	1	1	1	1	1	1	1	1
QC (S, D, B)				S				D				B
# of Environmental Samples	8	8	8	8	8	8	8	8	8	8	8	8
# of QC's	2	1	1	1	1	1	1	2	1	1	2	1

S = spike, D = split duplicate, B = blank

# of QC's = 15% of # of environmental samples; with 96 environmental samples, we have to collect 15 QC's

1 = first time site visited 2 = second time site visited

APPENDIX 3A

STANDARD OPERATING PROCEDURE FOR COLLECTING WATER SAMPLES IN THE SACRAMENTO RIVER BASIN

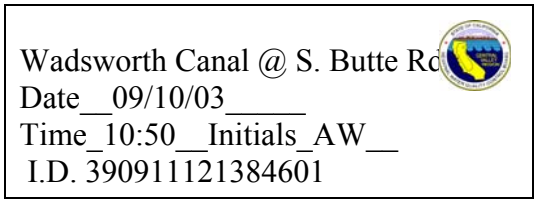
Standard Operating Procedure for Collecting Water Samples in the Sacramento River Basin

Overview of the sampling sites and sampling methods:
D = discharge measurements are taken at these locations
B = sampling will be done from a boat

Site 1	Sacramento River at Colusa	BRIDGE / 3L Teflon	
Site 3	Sacramento River at Tower Bridge	BRIDGE / D-77	**D / B**
Site 4	Colusa Basin Drain at Knights Landing	BRIDGE / 3L Teflon	**D**
Site 5	Sacramento River at Veterans Bridge	Boat / D-77	**D / B**
Site 6	Feather River near Verona	Boat / D-77	**D / B**
Site 7	Sacramento Slough	Boat / D-77	**D / B**

1. Labeling the sample bottle

- Use pre-printed labels for each site. The label should include the site name, ID number, date, sample time, and your initials
- Complete the printed label with an extra-fine-point Sharpie. Cover the entire label with a piece of clear tape to prevent peeling
- Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy



2. Check the Quality Control Schedule to see if a QC sample is scheduled for the site

If so, label an additional 1L amber glass bottle according to the instructions in Step 5 below. Read the QC sampling procedure before sampling.

3. Fill out Field Sheet at each sampling site

HOW TO FILL OUT A FIELD SHEET:

Sampling Information

- Sampling Type is already filled out. Add sampler initials
- Sampler Bottle: 1L amber bottles are glass, 3L bottles are Teflon
- Nozzle Material: use only if you sample with the D77
- Sampling Method: vertical integrated grab is from a bridge, grab is from the bank
- Stage: will become apparent with experience, also can be researched later on the web or read from a staff gage if present

Sample Collected

- If a quality control sample is scheduled, place a check beside type of sample
- Split will not be used unless accompanied by someone from the Regional Water Quality Control Board
- Sampling Time: Record rounded sample time

Field Measurements

Use Oakton pH/conductivity/temp meters; allow the probe to soak in native water for a few minutes for the reading to stabilize. Note the values for temperature, pH and EC on the field sheet along with the appropriate units (e.g. ^{o}C ,mS, µS,).

- BANK SAMPLE: measure directly from river edge
- BRIDGE SAMPLE: If you have an Oakton meter with a 100' probe, measure the parameters directly in the river at the center of the channel. If not, use the following procedure: after pouring off the sample use excess water from the 3L Teflon bottle for the field measurements; rinse the probe and plastic container with water from the 3L bottle before pouring another portion into the measuring container. Measure water parameters immediately after pouring off the sample so that conditions (temperature) do not change
- Flow and stage fields will be completed in the lab by getting information from CDEC or USGS web sites; please note source, date of receiving the information and your initials on the field sheet

At the end of the day fill the electrode storage cap with electrode storage solution before placing the meter in its case.

Recalibrate the Oakton pH/conductivity/temp meters once per month. Record recalibration date on a piece of labeling tap and affix to the inside panel of the meter case.

Note anything significant or unusual under Observations on the field sheet; for example waste disposal, irrigation runoff, foam on water surface, dead fish, etc.

Original field sheets stay with UC Davis in a prepared folder at the IOE.

4. How to collect a sample

Always wear clean gloves during sampling procedure!

BANK

a) Using bungee cord, affix 1L amber glass bottle to sampling pole
   To attach 250mL ELISA bottle:
   - (i) slide bungee through grating with blue ball on the bottom
   - (ii) loop through grating
   - (iii) slip pre-attached white cord over bottle top
   - (iv) slip bungee over bottle top

B) CHECK TO INSURE THE BOTTLE IS SECURE

c) Remove the cap (wear clean glove!)
d) Immerse the bottle until bubbles stop. Fill completely; do not leave any headspace
e) Replace the cap (still wearing the clean glove!)
f) Rinse the outside of the bottle with deionized water
g) Slip the bottle into a protective sleeve
h) Place sample directly into a cooler (up to 15 1L bottles can be placed in one cooler). Make sure there is no glass-to-glass contact

BRIDGE SAMPLE

1. Put on your orange safety vest. Always be aware of traffic and use caution while sampling from a bridge
2. At the van, put the 3L Teflon bottle into the TECHMA cage, secure it with the bungee cord (you will loose the bottle, if the bungee cord is not strapped around the bottle!), and remove the cap
3. Wearing leather gloves, carefully lower the bottle from the bridge railing to the water surface. Do not lower too fast or the bottle may be propelled from the cage upon impact. Perform a triple rinse with native water. Fill the bottle at least ¼ full for each rinse
4. To collect the sample, fill the bottle 1/4th at each of three equally spaced verticals (submerge for about 3-5 seconds), being careful to avoid contact between the bottle and anything but river water, especially when moving between verticals

5. Return to the van
6. Remove the 3L bottle from the TECHMA cage and swirl the water until completely mixed
7. The second person has already labeled the sample bottle. While wearing clean gloves the second person removes the bottle cap and holds the sample bottle as the sampler pours from the 3L Teflon bottle into the sample bottle. After the sample bottle is completely filled the second person then recaps the sample bottle
8. Rinse the outside of the sample bottle with deionized water, place the bottle in a protective sleeve and store it in the cooler.

The last thing to do before filling any amber glass sample bottle, regardless of method, is to remove the lid. The first thing to do after filling any amber glass sample bottle, regardless of method, is to replace the lid. If you have more than one sample bottle to fill, remove each lid just prior to filling the bottle

Clean the 3L bottle after sampling with the following procedure:

- While wearing gloves, add 10% Liquinox soap mixture (2-3 squeezes) and approximately 50ml of deionized water to the Teflon bottle. Place the cap on the bottle and swirl the soap around inside the bottle until the entire inside surface has been covered with suds. Un-cap the bottle and pour the soap onto the ground. Rinse the bottle and cap using deionized water until no suds remain inside the bottle or on the cap
- Poor 5-10ml of methanol into the bottle and swirl, with the cap on, until methanol has covered the entire inside surface of the bottle. Carefully pour the waste methanol into the methanol waste container. Seal the methanol bottle and waste container with Parafilm to prevent fume leakage. *Methanol is dangerous—do not inhale or touch!*

The 3L bottle is ready for the next sampling and should be stored, with the cap on, inside the TECHMA cage

5. If scheduled collect a quality control sample

View the QC Schedule to find out which type of QC sample you should collect that day

-- ***Field duplicate:***

a) Collect both samples simultaneously. If using a pole sampler place two bottles in the sampler. If using the TECHMA fill the 3L Teflon bottle with enough water for both the environmental and duplicate samples
b) Mark the sampling time of the duplicate sample by adding **3 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then duplicate time is 14:03). **Do not** indicate *duplicate* on the label or on the COC!

-- ***Matrix Spike:***
For the matrix spike sample add **9 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then spike time is 14:09) and mark as "matrix spike" on the **COC** *and* **label**. It should be made obvious so that the lab knows that this sample needs to be spiked.

BRIDGE SAMPLE

a) From the single 3L Teflon filled using the procedure above pour the collected water into two 1L bottles; one for the environmental sample and one for the matrix spike.

BANK SAMPLE

b) Fill two 1L bottles with one reach of the pole sampler; one for the environmental sample and one for the matrix spike.

-- ***Blank sample:***
Do not indicate blank on label or on COC. Time offset: add **1 minute** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then blank time is 14:01).

BRIDGE SAMPLE

BEFORE TAKING ENVIRONMENTAL SAMPLE:

a) Rinse the clean 3L Teflon bottle three times with deionized water (approximately 50ml for each rinse)
b) Fill the 3L bottle 2/3 full with deionized water and pour into a 1L bottle for the blank

BANK SAMPLE

Fill one 1L bottle with deionized water for the blank

Whoever did not fill out the field sheet and COC should double check all of the recorded times for completeness and error at the end of the sampling day

Check ice level

The temperature of the ice chest should be around 4°C. Make sure to add ice if necessary.

6. Deliver samples within 48 hours

Samples need to be dropped of at:

- **(1L amber glass bottles)**
  California Department of Food and Agriculture, Center for Analytical Chemistry, 3292 Meadowview Road, Sacramento, Ca 95832 Responsible Person: Stephen Siegel, (916) 275-3735 or ssiegel@cdfa.ca.gov
  open from 8 am to 5 pm after hours call Stephen Siegel,
  No drop off on weekends or on holidays unless pre-arranged! (For storage in our facility or somewhere else over the weekend make sure that there is enough ice in the cooler and the temperature stays around 4 degrees C)

- **(ELISA)**
  Samples will be delivered to the refrigerator in Room 114 of the Center for Aquatic Biology and Aquaculture at UC Davis. The original COCs will be left with the samples. Custody of samples will be relinquished to the Aquatic Ecosystems Analysis Laboratory analyst, Christine Fessler (530) 400-3227.

-

7. Complete Chain of Custody forms

Complete two Chain of Custody forms for each sampling day, one for the 1L amber glass bottles and one for the 250mL ELISA bottles.

- The original COCs for the 1L amber glass bottles will stay in the CDFA Lab. Be sure to have Steve Siegel (or other recipient) make you a copy of the COC. Upon return to the IOE fax a copy of the COC to Danny McClure within 24 hours (FAX: (916) 464-4779) then place our copy of the COC in the prepared folder at the IOE. After faxing, put your name, date, and time of fax on the copy and file it
- 250ml Original COC's will stay at the RWQCB with the ELISA samples and one copy will be filed in a folder at the IOE

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes.
The document must have both yours **and** the lab's signature before faxing it to Danny.

APPENDIX 3B

STANDARD OPERATING PROCEDURE FOR COLLECTING WATER SAMPLES IN THE SACRAMENTO-SAN JOAQUIN DELTA

Standard Operating Procedure for Collecting Water Samples in the Sacramento-San Joaquin Delta

Table of contents:

1. Overview of the sampling sites and methods:

D = Discharge measurements are taken at these sites

Delta 2	Mosher Slough at Mariners Drive	BRIDGE / 3L Teflon
Delta 3	Five-Mile Slough at Plymouth Road	BANK—grab sample
Delta 4	Calaveras River at Ijams Road	BANK—grab sample
Delta 5	Mid Roberts Island Drain	BANK—grab sample
Delta 6	French Camp Slough at S. Manthey Road	BANK—grab sample
Delta 10	Ulatis Creek at Brown Road	BRIDGE / 3L Teflon **D**
Delta 11	Duck Slough	BANK—grab sample

2. Labeling the sample bottles

Use preprinted labels. The sample ID should have the following format:
DP YYMMDD-nn
DP (=Delta Pesticides)
YYMMDD = Year, Month, Day
nn = sample number in sampling order for each sampling day (01, 02, 03…)
Example: if, at the first site visited on January 20, 2004, a matrix spike is scheduled the environmental sample for that site would be labeled DP040120-01; and the spike would be labeled DP040120-02 Spike. The first sample collected at the next site would be labeled

DP040120-03, and so on. Notice that the date on the sample label is given in the order MMDDYY, while the sample ID is ordered YYMMDD-nn.

Date__09/10/04_____
Time_10:50**_Initials_**AW**_**
I.D. DP040910-01**_____**

- The label should include the sample ID, date, sample time, and your initials
- Complete the printed label with an extra-fine-point Sharpie. Cover the entire label with a piece of clear tape to prevent peeling
- Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy

3. Fill out one Field Sheet at each sampling site

HOW TO FILL OUT THE FIELD SHEET:

- Station ID: for example Delta01
- Station Name: Mokelumne River at New Hope Road
- Sampling time: rounded 24-hour military time (e.g. 14:00)

Sampling Information

- Sampling bottle: 1L amber bottles are glass, 3L bottles are Teflon
- Sample type: integrated grab is from bridge, grab is from bank
- Stage: will become apparent with experience, also can be researched later on web or read from a staff gage, if present

Sample Collected

- Write the sample ID for the environmental sample in the field labeled Field Sample
- If a quality control (QC) sample is scheduled, place a check beside the sample type required and record the sample ID for the QC

Always double check sample ID's on the field sheet, COC, and label. Sample ID's on the field sheets are the only way to identify the samples!

Field Measurements

Use Oakton pH/conductivity/temp meters; allow the probe to soak in native water for a few minutes until the reading stabilizes. Note the values for temperature, pH and EC on the field sheet along with appropriate units (e.g. mS, µS, ˚C).

- BANK: measure directly from the edge of the river
- BRIDGE: If you have an Oakton meter with a 100' probe, measure from the center of the channel. If the probe is not long enough to reach the water use the following procedure: after pouring off sample use excess water from the 3L Teflon bottle for the field measurements; rinse probe and plastic container with native water (from 3-L Teflon) before pouring another portion out of 3L bottle into the measuring container. Measure water parameters immediately after pouring off sample to avoid change in water temperature
- Flow and stage fields will be completed in the lab by compiling data from CDEC or USGS web sites; please note source, date that data was received and your initials on the field sheet

At the end of the day fill the electrode storage cap with electrode storage solution before placing the meter in its case.

Note anything significant or unusual under Observations on the field sheet; for example waste disposal, irrigation runoff, foam on water surface, dead fish, etc.

Original forms stay with UC Davis in a prepared folder at the IOE. At the end of each sampling day, field sheets are faxed to Jamie Lu (916) 464-4779.

Recalibrate Oakton pH/conductivity/temp meters once every month. Record recalibration date and your initials on a piece of labeling tape and affix to inside panel of meter case.

4. How to collect an environmental sample

Always wear clean gloves during the sampling procedure!

BANK
a) Using a bungee cord, affix a 1L amber glass bottle to the pole sampler
b) Check to insure the bottle is secure!
c) Remove the cap (wear clean glove!)
d) Immerse the bottle until bubbles stop. Fill completely; do not leave any headspace
e) Replace the cap (still wearing the clean glove!)
f) Rinse the outside of the bottle with deionized water
g) Slip the bottle into a foam sleeve
h) Place the sample directly into a cooler (up to 15 1L bottles can be placed in one cooler). Make sure there is no glass-to-glass contact.

BRIDGE SAMPLE

1. Put on your orange safety vest. Always be aware of traffic and use caution while sampling from a bridge.
2. At the van, put the 3L Teflon bottle into the TECHMA cage, secure it with the bungee cord (you will loose the bottle, if the bungee cord is not strapped around the bottle!), and remove the cap.
3. Wearing leather gloves, carefully lower the bottle from the bridge railing to the water surface. Do not lower too fast or the bottle may be propelled from the cage upon impact. Perform a triple rinse with native water. Fill the bottle at least ¼ full for each rinse
9. To collect the sample, fill the bottle 1/4th at each of three equally spaced verticals (submerge for about 3-5 seconds), being careful to avoid contact between the bottle and anything but river water, especially when moving between verticals
10. Return to the van
11. Remove the 3L bottle from the TECHMA cage and swirl the water until completely mixed
12. The second person has already labeled the sample bottle. While wearing clean gloves the second person removes the bottle cap and holds the sample bottle as the sampler pours from the 3L Teflon bottle into the sample bottle. After the sample bottle is completely filled, the second person then recaps the sample bottle
13. Rinse the outside of the sample bottle with deionized water, place the bottle in a protective sleeve and store it in the cooler.

The last thing to do before filling any amber glass sample bottle, regardless of method, is to remove the lid. The first thing to do after filling any amber glass sample bottle, regardless of method, is to replace the lid. If you have more than one sample bottle to fill, remove each lid just prior to filling the bottle

Use the following procedure to clean the 3L Teflon bottle after sampling:

- While wearing gloves, add 10% liquinox soap mixture (2-3 squeezes) and approximately 50ml of deionized water to the Teflon bottle. Place the cap on the bottle and swirl the soap around inside until the entire inside surface has been covered with suds. Un-cap the bottle and pour the soap onto the ground. Rinse the bottle and cap using deionized water until no suds remain inside the bottle or on the cap
- Poor 5-10ml of methanol into the bottle and swirl, with the cap on, until methanol has covered the entire inside surface of the bottle. Carefully pour the methanol into the methanol waste container. Cap the 3L bottle. Seal the methanol bottle and waste container with Parafilm to prevent fume leakage. *Methanol is dangerous—do not inhale or touch!*
- The 3L bottle is ready for the next sampling and should be stored, with the cap on, inside the TECHMA cage

5. How to collect a quality control sample

View the QC schedule to find out which type of QC sample you should collect that day

-- *Split duplicate:*

1. Collect both samples simultaneously. If using a pole sampler place two bottles in the sampler. If using the TECHMA fill the 3L Teflon bottle with enough water for both the environmental and duplicate samples
2. Mark the sampling time of the duplicate sample by adding **5 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then duplicate time is 14:05). **Do not** indicate *duplicate* on the label or on the COC.

-- *Matrix spike:*

For the matrix spike sample record the same sampling time as the environmental sample. Mark as "matrix spike" on the **COC** *and* **label**. It should be made obvious so that the analyzing lab knows that this sample needs to be spiked.

BRIDGE SAMPLE

From the 3L Teflon bottle filled using the above procedure, pour the collected water into two 1L bottles; one for the environmental sample and one for the matrix spike

BANK SAMPLE

Fill two 1L bottles with one reach of the pole sampler; one for the environmental sample and one for the matrix spike

-- *Blank sample:*

Do not indicate blank on label or on COC. Time offset: add **5 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then blank time is 14:05).

BRIDGE SAMPLE

BEFORE COLLECTING THE ENVIRONMENTAL SAMPLE:

1. Rinse the clean 3L Teflon bottle three times with deionized water (approximately 50ml for each rinse)
2. Fill the 3L bottle 2/3 full with deionized water and pour into a 1L amber glass bottle for the blank

BANK SAMPLE

Fill one 1L amber glass bottle with deionized water for the blank

-- *Equipment blank:*

One Equipment Blank needs to be taken the first time you use a new sampling pole. Clean a large bucket with 10% liquinox soap and deionized water (methanol is not necessary). Put

the clean bucket under the pole, rinse the pole using >2 liters deionized water. With the water collected in the bucket, fill a 1L bottle. Do not indicate "equipment blank" on the label or COC, however indicate this on the field sheet. No time offset necessary.

Whoever did not fill out the field sheet and COC will double check all of the recorded times for completeness and error at the end of the sampling day

Check ice level

The temperature of the ice chest should be 4°C. Make sure to add ice if necessary.

6. Delivering the samples within 48 hours

Samples need to be dropped of at:

California Department of Food and Agriculture:
Center for Analytical Chemistry, 3292 Meadowview Road, Sacramento, CA 95832
Responsible Person: Stephen Siegel, (916) 275-3735 or ssiegel@cdfa.ca.gov
open from 8 am to 5 pm, after hours call Stephen Siegel
No drop off on weekends or on holidays unless pre-arranged! (For storage in our facility or somewhere else over the weekend make sure that there is enough ice in the cooler and the temperature stays around 4 degrees C). All samples must be delivered within 48 hours of collection.

7. Completing Chain of Custody forms

Complete Chain of Custody forms for each sampling day

The original COC's will stay in the CDFA Lab. Be sure to have Steve Siegel (or other lab recipient) make you a copy of the COC. Upon return to the IOE fax a copy of the COC and the field sheets to Jamie Lu within 24 hours (FAX: (916) 464-4779). Place the hard copy in a prepared folder at the IOE. After faxing, write the date, time of fax and your initials on the upper right corner of each sheet before filing.

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes.
The document must have both your signature **and** the signature of the receiving person at the analytical lab before faxing it to Jamie.

APPENDIX 3C

STANDARD OPERATING PROCEDURE FOR COLLECTING WATER SAMPLES IN THE SAN JOAQUIN RIVER BASIN

Standard Operating Procedure for Collecting Water Samples in the San Joaquin River Basin

Overview of the sampling sites and sampling methods:

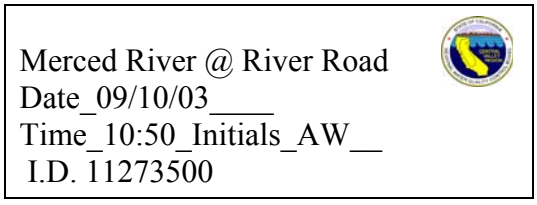
Site 6	San Joaquin River at Vernalis	BRIDGE / 3L Teflon
Site 7	Stanislaus River at Caswell State Park	BANK—grab sample
Site 5	Tuolumne River at Shiloh Road	BRIDGE / 3L Teflon
Site 1	Merced River at River Road	BRIDGE / 3L Teflon
Site 3	San Joaquin River at Crow's Landing	BANK—grab sample

These 5 sites should be sampled in the following order each day for four consecutive days:

San Joaquin River at Vernalis → Stanislaus River at CSP → Tuolumne River at Shilo Road → → Merced River at River Road → San Joaquin River at Crow's Landing → → Tuolumne River at Shilo Road →Stanislaus River at CSP → San Joaquin River at Vernalis → back

1. Labeling the sample bottle

- Use pre-printed labels for each site. The label should include the site name, site ID number, date, sample time, and your initials
- Complete the printed label with an extra-fine-point Sharpie. Cover the entire label with a piece of clear tape to prevent peeling.
- Use 24-hour military time for the sample time; round to the nearest 10 minutes. For example: a sample collected at 09:52 would have the sample time on the label and Chain of Custody (COC) form rounded off to 09:50; a sample collected at 09:57 would be rounded up to 10:00; 09:55 would also be rounded up to 10:00. Use the following format for the date: mm/dd/yy



2. Fill out one Field Sheet at each sampling site

HOW TO FILL OUT A FIELD SHEET:

Sampling Information

- Sampling Type is already filled out. Add sampler initials
- Sampler Bottle: 1L amber bottles are glass, 3L bottles are Teflon
- Sampling Method: vertical integrated grab is from a bridge, grab is from the bank
- Stage: will become apparent with experience, also may be researched later on the web or read from a staff gage if present

Sample Collected

- If a quality control sample is scheduled, place a check beside the type of sample
- Split will not be used unless accompanied by someone from the Regional Water Quality Control Board
- Sampling Time: Record rounded sample time

Field Measurements

Use Oakton pH/conductivity/temp meters; allow the probe to soak in native water for a few minutes for the reading to stabilize. Note the values for temperature, pH and EC on the field sheet along with the appropriate units (e.g. ^{o}C, mS, µS).

- BANK SAMPLE: measure directly from river edge
- BRIDGE SAMPLE: after pouring off the sample use excess water from the 3L Teflon bottle for the field measurements; rinse the probe and plastic container with water from the 3L bottle before pouring another portion into the measuring container. Measure water parameters immediately after pouring off the sample to avoid change in water temperature
- Flow and stage fields will be completed in the lab by getting information from CDEC or USGS web sites; please note source, date data was received and your initials on the field sheet

At the end of the day fill the electrode storage cap with electrode storage solution before placing the meter in its case.

Recalibrate the Oakton pH/conductivity/temp meters once per month. Record recalibration date on a piece of labeling tap and affix to the inside panel of the meter case.

Note anything significant or unusual under Observations on the field sheet; for example waste disposal, irrigation runoff, foam on water surface, dead fish, etc.

Original field sheets stay with UC Davis in a prepared folder at the IOE.

3. How to collect a sample

Always wear clean gloves during the sampling procedure!

BANK SAMPLE

a) Using bungee cord, affix a 1L amber glass bottle to the sampling pole

B) CHECK TO INSURE THE BOTTLE IS SECURE

c) Remove the cap (wear clean glove!)
d) Immerse the bottle until bubbles stop. Fill completely; do not leave any headspace
e) Replace the cap (still wearing the clean glove!)
f) Rinse the outside of the bottle with deionized water
g) Slip the bottle into a foam sleeve
h) Place sample directly into a cooler (up to 15 1L bottles can be placed in one cooler). Make sure there is no glass-to-glass contact

BRIDGE SAMPLE

Put on your orange safety vest. Always be aware of traffic and use caution while sampling from a bridge

1. At the van, put the 3L Teflon bottle into the TECHMA cage, secure it with the bungee cord (you will loose the bottle, if the bungee cord is not strapped around the bottle!), and remove the cap
2. Wearing leather gloves, carefully lower the bottle from the bridge railing to the water surface. Do not lower too fast or the bottle may be propelled from the cage upon impact. Perform a triple rinse with native water. Fill the bottle at least ¼ full for each rinse
3. To collect the sample, fill the bottle 1/4th at each of three equally spaced verticals (submerge for about 3-5 seconds), being careful to avoid contact between the bottle and anything but river water, especially when moving between verticals
4. Return to the van
5. Remove the 3L bottle from the TECHMA cage and swirl the water until completely mixed
6. The second person has already labeled the sample bottle. While wearing clean gloves the second person removes the bottle cap and holds the sample bottle as the sampler pours from the 3L Teflon bottle into the sample bottle. After the sample bottle is completely filled the second person then recaps the sample bottle
7. Rinse the outside of the sample bottle with deionized water, place the bottle in a protective sleeve and store it in the cooler.

The last thing to do before filling any amber glass sample bottle, regardless of method, is to remove the lid. The first thing to do after filling any amber glass sample bottle, regardless of method, is to replace the lid. If you have more than one sample bottle to fill, remove each lid just prior to filling the bottle

Clean the 3L bottle after sampling with the following procedure:

- While wearing gloves, add 10% liquinox soap mixture (2-3 squeezes) and approximately 50ml of deionized water to the Teflon bottle. Place the cap on the bottle and swirl the soap around inside until the entire inner surface has been covered with suds. Un-cap the bottle and pour the soap onto the ground. Rinse the bottle and cap using deionized water until no suds remain inside the bottle or on the cap
- Poor 5-10ml of methanol into the bottle and swirl - with the cap on - until methanol has covered the entire inside surface of the bottle. Carefully pour the waste methanol into the methanol waste container. Seal the methanol bottle and waste container with Parafilm to prevent fume leakage. *Methanol is dangerous—do not inhale or touch!*
- The 3L bottle is ready for the next sampling and should be stored, with the cap on, inside the TECHMA cage

4. If scheduled collect a quality control sample

View the QC Schedule to find out which type of QC sample you should collect that day

-- *Field duplicate*:

1. Collect both samples simultaneously. If using a pole sampler place two bottles in the sampler. If using the TECHMA fill the 3L Teflon bottle with enough water for both the environmental and duplicate samples
2. Mark the sampling time of the duplicate sample by adding **3 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then duplicate time is 14:03). **Do not** indicate *duplicate* on the label or on the COC!

-- *Matrix Spike:*

For the matrix spike sample add **9 minutes** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then spike time is 14:09) and mark as "matrix spike" on the **COC** *and* **label**. It should be made obvious so that the lab knows that this sample needs to be spiked.

BRIDGE SAMPLE

1. From the 3L Teflon, filled using the procedure above, pour the collected water into two 1L bottles; one for the environmental sample and one for the matrix spike.

BANK SAMPLE

2. Fill two 1L bottles with one reach of the pole sampler; one for the environmental sample and one for the matrix spike.

-- Blank sample:
Do not indicate blank on label or on COC. Time offset: add **1 minute** to the time of the environmental sample (e.g. environmental sample collected at 14:00 then blank time is 14:01).
BRIDGE SAMPLE
BEFORE TAKING ENVIRONMENTAL SAMPLE:

3. Rinse the clean 3L Teflon bottle three times with deionized water (approximately 50ml for each rinse)
4. Fill the 3L bottle 2/3 full with deionized water and pour into a 1L bottle for the blank.

BANK SAMPLE
Fill one 1L bottle with deionized water for the blank

Whoever did not fill out the field sheet and COC should double-check all of the recorded times for completeness and error at the end of the sampling day!

Check ice level

The temperature of the ice chest should be 4°C. Make sure to add ice if necessary.

5. Deliver the samples within 48 hours

Samples need to be dropped of at:

California Department of Food and Agriculture
Center for Analytical Chemistry, 3292 Meadowview Road, Sacramento, Ca 95832
Responsible Person: Stephen Siegel, (916) 262-1434 or ssiegel@cdfa.ca.gov
open from 8 am to 5 pm after hours call Stephen Siegel (916) 275-3735 cell.
No drop off on weekends or on holidays unless pre-arranged! (For storage in our facility or somewhere else over the weekend make sure that there is enough ice in the cooler and the temperature stays at 4 degrees C)

6. Complete Chain of Custody forms

Complete a Chain of Custody form for each sampling day.

The original COC's will stay in the CDFA Lab. Be sure to have Steve Siegel (or other lab recipient) make you a copy of the COC. Upon return to the IOE fax a copy of the

COC to Diane Beaulaurier within 24 hours (FAX: (916) 464-4779) then place our copy of the COC in the prepared folder at the IOE. After faxing, put your name, date, and time of fax on our copy and file it

Sample transfer between field staff and laboratory is documented by **signing and dating** "relinquished by" and "received by" blocks whenever sample possession changes.
The document must have both yours **and** the lab's signature before faxing it to Diane.

APPENDIX 4

STANDARD OPERATING PROCEDURE FOR VELOCITY MEASUREMENT AND DISCHARGE CALCULATION USING THE PRICE TYPE AA CURRENT METER WITH A WADING ROD OR A BRIDGE BOARD AND SOUNDING REEL

Standard Operating Procedure for
Velocity Measurement and Discharge Calculation
Using the Price Type AA Current Meter with a Wading Rod
or a Bridge Board and Sounding Reel
(Revised June 2004 HJC)

BACKGROUND

Stream discharge is the volume of water passing a cross-section per unit of time and is generally measured in cubic feet per second (cfs) or cubic meters per second (cms). The cross-sectional area is measured by stretching a tape across the stream to determine width, and recording depths using a wading rod or bridge board and sounding reel. For accuracy there should be a minimum of 20-30 verticals, or points, at which the velocity is measured in any particular stream, with no more than 10% of the total discharge in any rectangular subsection to ensure that a valid average discharge is measured. For measuring discharge, follow the steps below.

PROCEDURES

WADING ROD METHOD

1. Select a cross section that best meets the following criteria:
   - Converging flow (i.e., cross-sectional area decreasing downstream) without areas of near-zero velocity or eddies.
   - Absence of backwater conditions
   - Smooth cross section with minimal flow obstructions upstream or downstream.
   - Depth shallow enough to provide safe wading conditions.

   Remove any large stones, sticks, vegetation and other objects immediately upstream and downstream of the measurement section.
2. Stretch a tape between the endpoints (width) of the channel making sure that the tape is perpendicular to the banks of the stream. To obtain an accurate discharge measure at least 20-30 verticals. The verticals should be spaced so that no subsection has more than 10% (ideally 5%) of the total discharge. Equal widths of partial sections across the entire cross section are not recommended unless the discharge is well distributed. Make the width of the partial sections less as depths and velocities becomes greater. If the stream is small (e.g. < 4ft wide) then an approximation can be used to set the amount of verticals. For example, 15 verticals for a 4ft wide stream should be sufficient. On the field sheet record the reading from your tape at the right (REW) and left (LEW) water's edge of the channel.
3. Remove the meter from the protective carrying case. Check the pivot before using the meter. The point should be sharp and the pivot should be straight. If the pivot is damaged in any way replace it with the spare pivot. Check to make sure that the pivot was lubricated after the previous use. Use only one drop of oil on the pivot. See **Appendix B** for care and transport of current meter.
4. Perform a spin test of the bucket wheel. Holding the meter upright, with the pivot in a vertical position, spin the bucket wheel with your finger. The bucket wheel should spin, without additional help, for a minimum of two minutes before coming to rest. If the bucket wheel stops before two minutes, replace the pivot and perform another spin test. Ideally the spin test should be performed inside a vehicle or other closed space to prevent wind influence.
5. To ensure an accurate reading, the meter must be completely submerged under water and free of interference. Make notes about boulders, snags, pier influences or other obstructions that may bias the actual flow. Estimate the area influenced by these obstructions. Record on the discharge field sheet which bank you begin your measurements from by writing the abbreviations LEW (left edge water) or REW (right edge water) next to that vertical. Left and right banks are denoted facing downstream. Indicate on the note sheet the distance from the initial point to the edge of the water. Measure and record the depth at the edge of water. Record your start time.

6. Stand downstream from the flow meter, in a position that least affects the velocity of the water passing through the meter. Hold the rod with the meter directly facing the flow; ensuring the rod is vertical. If the stream flow is not perpendicular to the cross-section be sure to measure and record the angle coefficient using the markings on the edge of your discharge note.
7. If the depth is <2.5ft, measure velocity (V) once for each subsection at 0.6 times the total depth measured down from the water surface (e.g. if the depth = 2ft, position the torpedo at 1.2ft from the water's surface or 0.8ft from the bottom). Note that the staff is divided into tenths of a foot for easy calculation. If the depth is >2.5ft, measure V two times: at 0.2 and 0.8 times the total depth (e.g. if the depth = 3ft, measure at 0.6ft and 2.4ft from the water's surface). The average of these two readings is the V of the subsection.
8. Allow enough time between each reading (a minimum of 40 seconds for most meters) to obtain an accurate velocity. The operator calls out the distance, the depth, the velocity and the angle coefficient at each vertical. The note taker repeats back as it is recorded, as a check and balance system. For each vertical record depth, width, distance from the initial point, velocity, the observation depth (i.e. 0.2, 0.6, 0.8) and the angle coefficient (if there is one) on the discharge note. Continue this process as you move along the cross-section.
9. After measuring your last vertical record the distance from the initial point to the waters edge on the opposite bank. Record your end time.

BRIDGE BOARD AND SOUNDING REEL METHOD

1. Stretch a tape between the endpoints (width) of the bridge and mark the bridge railing permanently with a Sharpie or paint at every meter, making sure to allow for high water levels when marking. Your zero mark, or initial point, should be far enough back from the wetted edge to allow for expansion of the wetted edge during high flows. Measure the effective width (wet edge to wet edge) each time discharge is measured.
2. To obtain an accurate discharge use about 25 to 30 partial sections. With a smooth cross section and good velocity distribution, fewer sections may be used. Space the partial sections so that no partial section has more than 10 percent of the total discharge in it. The ideal measurement is one in which no partial section has more than 5 percent of the total discharge in it, but this is very seldom accomplished when 25 partial sections are used. Equal widths of partial sections across the entire cross section are not recommended unless the discharge is well distributed. Make the width of the partial sections less as depths and velocities becomes greater. Often, widths will need to be modified to accommodate for piers and other obstructions. Generally, where velocities are greater, widths are made smaller by the observer. See Appendix A for details concerning the affects of piers on width measurement.
3. Remove the meter from the protective carrying case. Check the pivot before using the meter. The point should be sharp and the pivot should be straight. If the pivot is damaged in any way replace it with the spare pivot. Check to make sure that the pivot was lubricated after the previous use. Use only one drop of oil on the pivot. See Appendix B for care and transport of current meter.
4. Perform a spin test of the bucket wheel. Holding the meter upright, with the pivot in a vertical position, spin the bucket wheel with your finger. The bucket wheel should spin, without additional help, for a minimum of two minutes before coming to rest. If the bucket wheel stops before two minutes, replace the pivot and perform another spin test. Ideally the spin test should be performed inside a vehicle or other closed space to prevent wind influence.
5. Setup the bridgeboard, sounding reel and current meter. Be sure to strap the bridge board to the bridge railing using the blue NRS strap! This is a necessary precaution to prevent accidental loss of the entire setup into the river. Use an appropriate sized sounding weight (faster velocities require heavier weights). We have 15, 30 and 50lb sounding weights. In most cases the 15lb sounding weight will be sufficient. If the meter begins to swim from side to side in the current switch to a heavier sounding weight. Be sure to attach the meter to the marked location on the suspension rod that corresponds with the weight you are using.
6. Place the bridgeboard and sounding reel at the first interval. Lower the sounding equipment until the centerline of the bucket wheel sits at the water's surface. Reset the depth-measuring device to zero

(Φ). Lower the sounding equipment to the bottom of the river and record the depth at the interval. Add the distance from the weight to the propeller assembly. For the 15 and 30lb sounding weights add 0.16m; for the 50lb sounding weight add 0.17m.

7. For each discharge measurement record the following information on the discharge note (USGS Form 9-275F):
    - Name of stream, location and site ID.
    - Date and crew
    - Time measurement was started using military time
    - Bank of stream that was the starting point
8. To ensure an accurate reading, the meter must be completely submerged under water and free of interference. Make notes about boulders, snags, pier influences or other obstructions that may bias the actual flow. Estimate the area influenced by these obstructions. Record on the field sheet which bank you begin your measurements from by writing the abbreviations LEW (left edge water) or REW (right edge water) next to that vertical. Left and right banks are denoted facing downstream. Indicate on the note sheet the distance from the initial point to the edge of the water. Measure and record the depth at the edge of water. Record your starting time.
9. After the depth is know and recorded, determine the method of velocity measurement. Normally the two-point method or the 0.6-depth method is used.

<u>The two-point method:</u>

- The two-point method is the one generally used by the US Geological Survey. This is the method we will be using for all of our verticals where the depth is greater than 0.76 m (2.5 feet). The two-point method is not used at depths less than 0.76 m (2.5 feet) because the current meter would be too close to both the water surface and the streambed to give dependable results. With the two-point method, observations of velocity are made at 0.2 and 0.8 of the depth below the water surface. The average of these two readings is the V of the subsection.

<u>Six-tenths-depth method:</u>

- With the 0.6-depth method, an observation of velocity made at 0.6 of the depth below the surface in the vertical is used as a mean velocity in the vertical. Actual observation and mathematical theory has shown that the 0.6-depth method provides reliable results and is used by the US Geological Survey under the following conditions:

    1. Whenever the depth is between 0.1 m (0.3 foot) and 0.76 m (2.5 feet).
    2. When the meter is placed a distance above the sounding weight, which makes it impossible to place the meter at the 0.8 depth. This circumstance prevents the use of the two-point method.

10. After the meter is placed at the proper depth, permit it to become adjusted to the current before starting the velocity measurement. The time required for such adjustment is usually only a few seconds if the velocities are greater than 0.3 mps, but for lower velocities, particularly if the current meter is suspended by a cable, a longer period of adjustment is needed. After the meter has become adjusted to the current, count the number of revolutions made by the rotor for a period of 40-70 seconds.
11. The operator calls out the distance, the depth, and the V. The note taker repeats back as it is recorded, as a check and balance system. For each vertical record depth, width, distance from the initial point, number of revolutions, observation depth (i.e. 0.2, 0.6, 0.8), and angle coefficient on the discharge note. Determine the angle coefficient at each vertical by measuring the angle of the weight in relation to the riverbank using the markings on the edge of the discharge note.
12. Move to each of the verticals and repeat this procedure; record the distance from initial point, depth, meter-position depth, revolutions, and time interval, until the entire cross section has been traversed. After measuring your last vertical record the distance from the initial point to the waters edge on the opposite bank. Record your end time.
13. If the bridge is not perpendicular to the river determine an overall bridge coefficient.

DISCHARGE CALCULATIONS

1. To obtain discharge: multiply each depth (ft or m) by the width (ft or m) of each interval, to yield the subsection area (ft^2 or m^2). Next, multiply the area by the velocity to obtain the discharge (cfs or cms) for the interval. Finally, sum all the discharge measurements across the width of the river; this will yield the total discharge of the river. If the subsection depth was >2.5ft (0.76m), then the V was taken at 0.2 and 0.8 times the total depth. Therefore, the V at 0.2 and 0.8 times the subsection depth should be averaged to yield a single V measurement before multiplying the V by the area of the subsection.
2. It is important to use the same units of measure in the field to ensure the accuracy of the flow measurements. For example, if the depth is measured in tenths, then the width should be measured in tenths for accuracy.
3. Use an Excel spreadsheet to calculate the discharge at each site. View examples from the 2002 TMDL project.

Use the following equations to calculate velocity (V):

1. For feet per second: V = 2.2048 R + 0.0178 (R=revolutions per second)*
2. For meters per second:
    - If less than 40 revolutions then: ((rev/seconds) x 2.18 + .02) x .3048 = MPS
    - If more than 40 revolutions then: ((rev/seconds) x 2.17 + .03) x .3048 = MPS

* Important: R = revolutions per second NOT the total # of revolutions.

Appendix A:
Bridges are often used for making discharge measurements of streams that cannot be waded. Measurement cross sections under bridges are often satisfactory for current-meter measurements. No set rule can be given for choosing between the upstream or downstream side of the bridge for making a discharge measurement. The advantages of using the upstream side of the bridge are:

- Hydraulic characteristics at the upstream side of bridge openings usually are more favorable.
- Approaching drift can be seen and thus can be more easily avoided.
- The streambed at the upstream side of the bridge is not likely to be scoured as badly as the downstream side.

The advantages of using the downstream side of the bridge are:

- Vertical angles are more easily measured because the sounding line will move away from the bridge.

- The flow lines of the stream may be straightened by passing through a bridge opening with piers.

Whether to use the upstream side or the downstream side of a bridge for a current-meter measurement should be decided individually for each bridge after considering the above factors. Other pertinent factors relate to physical conditions at the bridge, such as location of the walkway, traffic hazards, and accumulation of trash on pilings and piers.
Where piers are in the measuring section, it is usually necessary to use more than 25-30 subsections to obtain results as reliable as those obtained with a similar measuring section that has no piers. Piers not only affect the horizontal distribution of velocities, but they frequently affect the direction of the current, causing horizontal angles that must be carefully measured.
Whether or not to exclude the area of a bridge pier from the area of the measurement cross section depends primarily on the relative locations of the measurement section and the end of the pier. If measurements are made from the upstream side of the bridge, it is the relative location of the upstream end (nose) of the pier that is relevant; for measurements made from the downstream side it is the location of the downstream end (tail) of the pier that is relevant. If any part of the pier extends into the measurement cross section, the area of the pier is excluded. However, bridges quite commonly have cantilevered walkways from which discharge measurements are made. In that case the measurement cross section lies beyond the end of the pier-upstream from the nose or downstream from the tail, depending on which side of the bridge is used. In that situation it is the position and direction of the streamlines that determines whether or not the pier area is to be excluded. The hydrographer, if he had not previously noted the stationing of the sides of the pier when projected to the measurement cross section, does so now. If there is negligible or no downstream flow in that width interval (pier subsection)-that is, if only stagnation and (or) eddying exists upstream from the nose or downstream from the tail, whichever is relevant-the area of the pier is excluded. If there is significant downstream flow in the pier subsection, the area of the pier is included in the area of the measurement cross section. The horizontal angles of the streamlines in and near the pier subsection will usually be quite large in that circumstance.

Appendix B:

CURRENT METER CARE AND TRANSPORT

- Rinse current meter in clear water as soon as possible after use and dry using a soft cloth
- Never place a wet current meter in its carrying case
- Lubricate after 8 hours use or at least once a week when use is infrequent (see instructions)
- Always transport current meter in its protective case.
- Before placing meter in protective case raise bucket wheel with knurled brass nut to provide clearance between pivot and pivot bearing (see directions). Do not over-tighten nut as that may bend the pivot.
- After lubricating meter make sure to adjust pivot (see directions).

APPENDIX 5

OAKTON PORTABLE WATERPROOF pH/CON 10 METER CALIBRATION STANDARD OPERATING PROCEDURE

Aquatic Ecosystems Analysis Laboratory
John Muir Institute of the Environment
University of California, Davis
1490 Drew Avenue, Suite 150
Davis, CA 95616

OAKTON Portable Waterproof pH/CON 10 Meter Calibration Standard Operating Procedure

JMIE January 2004

Purpose: This standard operation procedure (SOP) provides a detailed description for the calibration of the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02)

Note: All calibrations used pH/conductivity/temperature probes designed for the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02) only.

Step 1: Reset pH and conductivity to the factory defaults.

To reset pH, make sure the meter is in pH mode, then:

1.) While in measurement mode, press CAL/MEAS and hold for 3 seconds.
2.) The meter will prompt RST in the upper display and CAL in the lower display.
3.) Press enter to reset the meter to its factory defaults. The screen will flash all characters, then return to measurement mode once the meter is reset.

To reset conductivity, make sure the meter is in conductivity mode, and then follow steps 1-3 above.

Step 2: Preparing the pH/CON meter for calibration.

1.) Remove the protective rubber cap of the probe before calibration.
2.) Wet the probe in tap water for 10 minutes before calibrating or taking readings to saturate the pH electrode surface and minimize drift.

Step 3: 3-point (OAKTON pH 4.00, 7.00 and 10.00) pH calibration.

1.) If necessary, press the MODE key to select pH mode. The pH indicator appears in the upper right hand corner of the display.
2.) Rinse the probe thoroughly with de-ionized water or a rinse solution. Do not wipe the probe; this causes a build-up of electrostatic charge on the glass surface.
3.) Dip the probe into the calibration buffer. The end of the probe must be completely immersed into the sample. Stir the probe gently to create a homogenous sample.
4.) Wait for the measured pH value to stabilize. The READY indicator will display when the reading stabilizes.
5.) Press CAL/MEAS to enter pH calibration mode. The primary display will show the measured reading, while the smaller secondary display will indicate the pH standard buffer solution. Scroll up or down until the secondary display value is the same as the pH buffer value you are using (pH 4.00, 7.00 or 10.00).
6.) Wait for the measured pH value to stabilize. The READY indicator will display when the reading stabilizes.

7.) After the READY indicator turns on, press ENTER to confirm calibration. A confirming indicator (CON) flashes and disappears. The meter is now calibrated at the buffer indicated in the secondary display.
8.) The secondary display automatically scrolls to the next buffer calibration option. Scroll up or down to select the next buffer value you want to calibrate (pH 4.00, 7.00 or 10.00).
9.) Rinse the probe with de-ionized water or a rinse solution, and place it in the next pH buffer.
10.) Follow steps 5-8 for additional calibration points.
11.) When calibration is complete, press CAL/MEAS to return to pH measurement mode.

Note: If the selected buffer value is not within +/-1.00 pH from the measured value: the electrode and buffer icon blink and the ERR annunciator appears in the lower left corner of the display. These indicators also flash if the buffer used in not the same as the buffer value on the secondary display.

Step 4: Conductivity Calibration

1.) Pour out two separate portions of the calibration standard and one of deionized water into separate clean containers. Choose a calibration solution value that is approximately 2/3 the full-scale value of the measurement range (e.g. in the 0 to 1999 µS range, use a 1413 µS solution for calibration). A 447 µS standard solution is generally adequate in this study.
2.) If necessary, press the MODE key to select the Conductivity Mode. The µS or mS indicator will appear on the right side of the display.
3.) Rinse your probe with deionized water, then rinse the probe in one of the portions of calibration standard.
4.) Immerse the probe into the second portion of calibration standard. The meter's autoranging function selects the appropriate conductivity range (four ranges are possible). Be sure to tap the probe to remove air bubbles. Air bubbles will cause errors in calibration.
5.) Wait for the reading to stabilize. The READY indicator lights when the reading is stable.
6.) Press the CAL/MEAS key. The CAL indicator appears above the primary display. The primary display shows the factory default and the secondary display shows the temperature.
7.) Scroll up or down to the value of your conductivity standard. Press and hold the scroll keys to go faster. The meter automatically compensates for temperatures using a factor of 2.00% per C.
8.) Press the ENTER key to confirm calibration. Upon calibration, the CON indicator appears briefly. The meter automatically switches back into Measurement mode. The display now shows the calibrated, temperature compensated conductivity value.

9.) For calibration in other ranges (Maximum: 4 ranges) repeat steps 1 through 9 with the appropriate calibration standards.

Note: if the calibration value input into the meter is different from the factory default value displayed by more than 30%, the ERR annunciator appears in the lower left corner of the display. Clean probe with alcohol. Verify that your calibration standard is fresh and accurate.

Step 5: Calibration Documentation

1.) After calibrating a meter for pH and conductivity, the person who calibrated the meter will record the date, which calibrations were made and their initials on a decal affixed to the inside of the meter case.

*Steps were transposed from the OAKTON Portable Waterproof pH/CON 10 Meter (Model #35630-02) manual of operating instructions (68X230403 rev2 01 / 02).

APPENDIX 6

MULTI-RESIDUE METHOD FOR EXTRACTION AND ANALYSIS OF PESTICIDES IN SURFACE WATER

Multi-Residue Method for Extraction and Analysis of Pesticides in Surface Water

1. Scope: To provide a standard procedure for the extraction and analysis of a broad range of pesticides in surface water using a Mass selective detector (MSD).

2. **Outline**:

- Apparatus
  - Reagents and Supplies
  - Method of Sample Preparation
- Methods of Analysis

3. **References**:

Methods of Analysis by the US Geological Survey National Water Quality Laboratory-Determination of Pesticides in Water by C18 SPE and capillary-Column GC/MS with SIM. By Steven D. Zaugg. *et el*

U. S. ENVIRONMENTAL PROTECTION AGENCY. 1971. Method for Organic Pesticides in Water and Wastewater. National Environmental Research Center. Cincinnati. Ohio

STANDARD METHODS For The EXAMINATION OF WATER AND WASTEWATER. 18th EDITION 1992. 6630 ORGANOCHLORINE PESTICIDES 6-101

4. **Specific Procedures**:

4.1 Apparatus

- 2-liter size Separatory Funnels
- 250 mL roundbottom flasks
- Glass Filter Funnel with glass wool and Na2SO4
- Rotavapor evaporator
- Nitrogen evaporator
- VWR vrtex genie or equivalent
- 15 mL collection tubes
- Agilent Model 5973 GC-MSD operated in SIM mode
- Vacuum apparatus with funnels and collection containers

4.2 Reagents and Supplies

- Methylene Chloride, nanograde or equivalent pesticide grade.
- Glass wool

- NaCl: Certified A.C.S. (Fisher Chemical)
- 0.45µ nylon filters (Alltech 2024 or equivalent)
- Sodium sulfate/ Methylene chloride rinsed and dried.

4.3 Method of Sample Preparation:

4.3.1 For MSD analysis:

a) Weigh and record the 1-liter size water sample.
b) Spike using 500µL surrogate spiking solution: 0.25µg/mL Chlorpyrifos methyl.
c) For the spike sample: spike 500µL appropriate spike solution. .
d) Empty approximately 500mL of the sample into a 2-liter size separatory funnel. Weigh and record the sample bottle. Add in approx 10-15 g of granular sodium chloride. Shake gently to dissolve salt.
e) Add in 60ml of methylene chloride. Shake well for three minutes. Let settle until the lower methylene chloride layer is completely separated from the above water layer. Filter bottom organic layer through a bed of granular anhydrous sodium sulfate (approx. 20g) into 250ml round bottom flask.
f) Repeat step e above two more times. Place round bottom flask on Rotavapor evaporator and evaporate to 5-7 mL's at 40° C. Transfer contents of round bottom flask to a 15mL collection tube. Rinse round bottom flask with 5ml methylene chloride and add to collection tube. Place 15mL collection tube on N-Evaporator with water temperature set at 40°C. Evaporate the sample to just dryness. Remove sample from N-Evaporator and carefully add 0.5ml of methylene chloride and 5.0µL of 5.0µg/mL internal standard solution into test tube with sample. Vortex and transfer into autosampler vial. Cap and store vials in -5^{0}C freezer until ready for analysis.

4.4 **Method of analysis**:

4.4.1 For GC-MSD: Agilent Model 5973 GC-MSD

a) GC Parameters:

GC Column: HP-5MS or equivalent; 30meter; 0.25mm x 0.25um film thickness.
Injector temperature initial at 230C
Injection Volume = 2ul

b) GC-MSD Parameters:

Selective Ion Monitoring Mode
EM Voltage: Abs 3000Volt (Max)
Tune & Tune file: Max. Sensitivity Auto Tune

c) Pesticides Monitored:

	LOD ppb	LOQ ppb
Eptam (EPTC)	0.020	0.05
Simazine	0.005	0.20
Diazinon	0.007	0.02
Carbaryl	0.007	0.02
Metalochlor	0.007	0.02
Chlorpyrifos	0.004	0.01
Cyanazine	0.007	0.05
Dacthal (DCPA)	0.007	0.05
Methidathion	0.010	0.03
Propargite	0.15	0.50
Azinphos methyl	0.007	0.05

Surrogate: Chlorpyrifos methyl- 250ppt
Internal standard: Anthracene-d10, Pyrene-d10, & Chrysene-d12 (500ppt)

d) Selective Ion Monitoring Parameters:

The Segment Start Time and SIM ions needed to be updated by the operation chemist from time to time due to instrument conditions or whenever new compounds are added or deleted. Maximum SIM Ions allowed per segment time is 30.

Total SIM Segments: 6

Group 1	Start Time:	4.00				
	SIM Ions:	86	128	164	173	(7)
		186	189	201		
Group 2	Start Time:	15.50				
	SIM Ions:	88	115	125	137	(13)
		144	179	186	188	
		201	274	286	288	
		304				
Group 3	Start Time:	19.50				
	SIM Ions:	162	197	198	204	(10)
		238	240	258	301	
		314	332			
Group 4	Start Time:	23.00				
	SIM Ions:	85	125	145		(3)
Group 5	Start Time:	26.00				
	SIM Ions:	77	132	135	141	(12)
		160	165	166	173	
		181	209	240	350	
Group 6	Start Time:	32.00				
	SIM Ions:	163	165	167	181	
		225	226	419		

TEMPERATURE:

Injector Temperature. 230c

Oven Temperature Programming:

Initial temperature 70C hold for 2.00 min.

Level	Rate (c/min)	Final temperature (c)	Final time
1	25	150	0.0
2	3	200	0.0
3	8	280	12.0

a) Method calibration
Five levels of standards are prepared in matrix of reagent grade water to calibrate the analysis method. A linear regression is used including 0,0. The R squared value should be greater or equal to 0.99. Standards are run with the sample set to check for calibration integrity. Continuing calibration standard values should be within ±25% of calibration. Residue concentration is taken from instrument report table and calculated. If the residue amount falls outside the calibration curve, the sample will be diluted and reanalyzed.

$$\text{Residue amount (ppt)} = \text{instrument amount} \times \frac{500\ (g)}{\text{Weight of sample}}$$

If R squared value of calibration curve is < 0.99, the pesticide level may be determined by direct comparison of residue response to the average response of the nearest bracketing standard concentration. Response of bracketing standards should not vary more than 25%. The residue response should fall within ±30% of standard response. If the residue amount falls outside calibration curve, the sample will be diluted and reanalyzed. A non-linear calibration may be necessary to achieve low detection limits or address specific instrumental techniques. Non-linear calibration is not to be used to compensate for detector saturation or to avoid instrument maintenance.

Calculation using single point comparisons:

$$\text{Sample amount (ppt)} = \frac{\text{Sample response}}{\text{Avg response of bracketing Standards}} \times \frac{500\ (g)}{\text{WT of sample (g)}} \times \text{standards amount (equivalent ppt)}$$

Surrogate: Chlorpyrifos methyl- 250ppt

4.5 Method Verification

Level 1 Day 1

Compound	Std. Conc.	Std before ppb	Std after Ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	50	63.07	62.87	0.3	62.97	26.96	42.8
Simazine	200	163.39	154.22	5.8	158.805	128.63	81.0
Diazinon	20	21.89	20.37	7.2	21.13	16.31	77.2
Chlorpyrifos methyl	50	43.68	40.86	6.7	42.27	32.94	77.9
Carbaryl	20	18.4	17.56	4.7	17.98	15.45	85.9
Metolachlor	20	22.44	21.23	5.5	21.835	18.02	82.5
Chlorpyrifos	10	6.84	6.19	10.0	6.515	5.65	86.7
Cyanazine	50	46.63	42.77	8.6	44.7	38.03	85.1
Dacthal (DCPA)	50	55.55	54.2	2.5	54.875	43.85	79.9
Methidathion	30	24.5	21.44	13.3	22.97	19.61	85.4
Propargite	500	395.81	365.33	8.0	380.57	304.01	79.9
Azinphos methyl	50	38.57	39.49	-2.4	39.03	31.06	79.6

Level 3 Day 1

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	200	207.87	204.84	1.5	206.355	91.8	44.5
Simazine	800	764.11	741.1	3.1	752.605	596.71	79.3
Diazinon	100	117.91	109.53	7.4	113.72	83.7	73.6
Chlorpyrifos methyl	200	181.72	171.92	5.5	176.82	130.78	74.0
Carbaryl	100	110.86	109.51	1.2	110.185	84	76.2
Metolachlor	100	130.04	124.47	4.4	127.255	104.38	82.0
Chlorpyrifos	50	35.22	34.16	3.1	34.69	27.46	79.2
Cyanazine	200	160.66	154	4.2	157.33	127.43	81.0
Dacthal (DCPA)	200	188.63	188.16	0.2	188.395	146.59	77.8
Methidathion	100	96.13	88	8.8	92.065	75.08	81.6
Propargite	1000	894.36	876.05	2.1	885.205	752.51	85.0
Azinphos methyl	200	153.05	144.27	5.9	148.66	123.84	83.3

Level 5 Day 1

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	1000	949.89	954.86	-0.5	952.375	433.73	45.5
Simazine	1200	1277.66	1206.8	5.7	1242.23	986.37	79.4
Diazinon	1000	976.27	923.75	5.5	950.01	712.86	75.0
Chlorpyrifos methyl	1000	938.06	906.41	3.4	922.235	667.62	72.4
Carbaryl	1000	989.33	747.69	27.8	868.51	750.72	86.4
Metolachlor	1000	934.85	886.54	5.3	910.695	717.68	78.8
Chlorpyrifos	500	502.41	477.94	5.0	490.175	375.71	76.6
Cyanazine	1000	998.22	1003.03	-0.5	1000.625	783.29	78.3
Dacthal (DCPA)	1000	965.57	976.13	-1.1	970.85	731.6	75.4
Methidathion	1000	976.54	873.36	11.2	924.95	733.07	79.3
Propargite	2000	2200.46	2213.68	-0.6	2207.07	1624.18	73.6
Azinphos methyl	1000	990.91	849.49	15.4	920.2	674.09	73.3

Level 1 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	50	62.87	63.6	-1.2	63.24	54.34	85.9
Simazine	200	154.22	162.91	-5.5	158.57	155.38	98.0
Diazinon	20	20.37	21.54	-5.6	20.96	21.97	104.8
Chlorpyrifos methyl	50	40.86	43	-5.1	41.93	41.23	98.3
Carbaryl	20	17.56	19.45	-10.2	18.51	19.35	104.6
Metolachlor	20	21.23	21.6	-1.7	21.42	21.07	98.4
Chlorpyrifos	10	6.19	6.2	-0.2	6.20	6.64	107.2
Cyanazine	50	42.77	46.75	-8.9	44.76	46.27	103.4
Dacthal (DCPA)	50	54.2	55.1	-1.6	54.65	53.91	98.6
Methidathion	30	21.44	23.14	-7.6	22.29	24.07	108.0
Propargite	500	365.33	416.06	-13.0	390.70	410.92	105.2
Azinphos methyl	50	39.49	41.11	-4.0	40.30	47.88	118.8

Level 3 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	200	204.84	207.68	-1.4	206.26	127.47	61.8
Simazine	800	741.1	750.43	-1.3	745.765	712.57	95.5
Diazinon	100	109.53	111.3	-1.6	110.415	106.99	96.9
Chlorpyrifos methyl	200	171.92	175.16	-1.9	173.54	161.52	93.1
Carbaryl	100	109.51	102.83	6.3	106.17	96.76	91.1
Metolachlor	100	124.47	124.56	-0.1	124.515	123.21	99.0
Chlorpyrifos	50	34.16	36.5	-6.6	35.33	33.99	96.2
Cyanazine	200	154	154.18	-0.1	154.09	156.29	101.4
Dacthal (DCPA)	200	188.16	186.78	0.7	187.47	180.96	96.5
Methidathion	100	88	86.66	1.5	87.33	84.67	97.0
Propargite	1000	876.05	850.46	3.0	863.255	822.54	95.3
Azinphos methyl	200	144.27	139.33	3.5	141.8	148.53	104.7

Level 5 Day 2

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	1000	954.86	949.22	0.6	952.04	690.4	72.5
Simazine	1200	1206.8	1222.11	-1.3	1214.455	1209.03	99.6
Diazinon	1000	923.75	961.76	-4.0	942.755	898.6	95.3
Chlorpyrifos methyl	1000	906.41	913.68	-0.8	910.045	858.32	94.3
Carbaryl	1000	947.69	875.18	8.0	911.435	879.64	96.5
Metolachlor	1000	886.54	892.46	-0.7	889.5	878.99	98.8
Chlorpyrifos	500	477.76	484.31	-1.4	481.035	473.38	98.4
Cyanazine	1000	1003.03	957.69	4.6	980.36	985.87	100.6
Dacthal (DCPA)	1000	976.13	953.99	2.3	965.06	925.06	95.9
Methidathion	1000	873.36	841.7	3.7	857.53	884.36	103.1
Propargite	2000	2213.68	1960.49	12.1	2087.085	2131.15	102.1
Azinphos methyl	1000	849.49	807.21	5.1	828.35	997.29	120.4

Level 1 Day 3

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	50	71.05	71.59	-0.8	71.32	57.03	80.0
Simazine	200	161.99	172.25	-6.1	167.12	141.4	84.6
Diazinon	20	22.11	23.07	-4.2	22.59	21.34	94.5
Chlorpyrifos methyl	50	49.55	51.55	-4.0	50.55	42.85	84.8
Carbaryl	20	23.86	27.11	-12.8	25.485	19.82	77.8
Metolachlor	20	25.49	27.7	-8.3	26.595	23.18	87.2
Chlorpyrifos	10	6.6	6.43	2.6	6.515	5.69	87.3
Cyanazine	50	48.41	54.71	-12.2	51.56	44.3	85.9
Dacthal (DCPA)	50	62.47	63.86	-2.2	63.165	55.8	88.3
Methidathion	30	30.97	34.02	-9.4	32.495	25.09	77.2
Propargite	500	492.2	524.97	-6.4	508.585	333.79	65.6
Azinphos methyl	50	61.64	66.16	-7.1	63.9	48.07	75.2

Level 3 Day 3

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	200	241.51	245.78	-1.8	243.645	89.36	36.7
Simazine	800	861.72	822.15	4.7	841.935	581.61	69.1
Diazinon	100	142.65	137.29	3.8	139.97	96.19	68.7
Chlorpyrifos methyl	200	228.46	220.89	3.4	224.675	149.7	66.6
Carbaryl	100	160.2	142.63	11.6	151.415	112.14	74.1
Metolachlor	100	170.09	165.99	2.4	168.04	126.69	75.4
Chlorpyrifos	50	41.58	37.04	11.5	39.31	26.56	67.6
Cyanazine	200	201.99	186.77	7.8	194.38	143.89	74.0
Dacthal (DCPA)	200	230.1	228.09	0.9	229.095	174.03	76.0
Methidathion	100	139.22	126.9	9.3	133.06	99.62	74.9
Propargite	1000	1172.44	1044.98	11.5	1108.71	828.31	74.7
Azinphos methyl	200	241.31	210.59	13.6	225.95	340.4	150.7

Level 5 Day 3

Compound	Std. Conc.	Std before ppb	Std after ppb	% Diff.	Average ppb	Sample ppb	% recovery
EPTC (Eptam)	1000	1115.44	1106.25	0.8	1110.845	757.42	68.2
Simazine	1200	1296.962	1408.62	-8.3	1352.791	1077.03	79.6
Diazinon	1000	1173.82	1221.56	-4.0	1197.69	946.29	79.0
Chlorpyrifos methyl	1000	1129.67	1193.45	-5.5	1161.56	882.91	76.0
Carbaryl	1000	1162.97	1414.12	-19.5	1288.545	1048.09	81.3
Metolachlor	1000	1156.79	1235.73	-6.6	1196.26	959.17	80.2
Chlorpyrifos	500	513.18	554.31	-7.7	533.745	423.76	79.4
Cyanazine	1000	1148.15	1218.92	-6.0	1183.535	980.75	82.9
Dacthal (DCPA)	1000	1123.9	1148	-2.1	1135.95	937.57	82.5
Methidathion	1000	1176.09	1448.52	-20.8	1312.305	976.82	74.4
Propargite	2000	2180.32	2496.83	-13.5	2338.575	1865.54	79.8
Azinphos methyl	1000	1118.15	1423.93	-24.1	1271.04	937.16	73.7

Level 1
All compounds at our LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	50	42.8	85.9	80.0	69.6	46.7	23.4
Simazine	200	81.0	98.0	84.6	87.9	4.5	9.0
Diazinon	20	77.2	104.8	94.5	92.2	69.7	13.9
Chlorpyrifos methyl	50	77.9	98.3	84.8	87.0	20.8	10.4
Carbaryl	20	85.9	104.6	77.8	89.4	68.7	13.7
Metolachlor	20	82.5	98.4	87.2	89.4	40.8	8.2
Chlorpyrifos	10	86.7	107.2	87.3	93.7	116.7	11.7
Cyanazine	50	85.1	103.4	85.9	91.5	20.7	10.3
Dacthal (DCPA)	50	79.9	98.6	88.3	88.9	18.7	9.4
Methidathion	30	85.4	108.0	77.2	90.2	53.2	16.0
Propargite	500	79.9	105.2	65.6	83.6	4.0	20.1
Azinphos methyl	50	79.6	118.8	75.2	91.2	48.0	24.0

Level 3
All compounds at aprox 4 times LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	200	44.5	61.8	36.7	47.7	6.4	12.8
Simazine	800	79.3	95.5	69.1	81.3	1.7	13.3
Diazinon	100	73.6	96.9	68.7	79.7	15.1	15.1
Chlorpyrifos methyl	200	74.0	93.1	66.6	77.9	6.8	13.7
Carbaryl	100	76.2	91.1	74.1	80.5	9.3	9.3
Metolachlor	100	82.0	99.0	75.4	85.5	12.2	12.2
Chlorpyrifos	50	79.2	96.2	67.6	81.0	28.8	14.4
Cyanazine	200	81.0	101.4	74.0	85.5	7.1	14.2
Dacthal (DCPA)	200	77.8	96.5	76.0	83.4	5.7	11.4
Methidathion	100	81.6	97.0	74.9	84.5	11.3	11.3
Propargite	1000	85.0	95.3	74.7	85.0	1.0	10.3
Azinphos methyl	200	83.3	104.7	150.7	112.9	17.2	34.4

Level 5
All compounds at aprox 20 times LOQ

Compound	Std. Conc.(ppt)	Day 1	Day 2	Day 3	Average Recovery	% RSD	SD
EPTC (Eptam)	1000	45.5	72.5	68.2	62.1	1.5	14.5
Simazine	1200	79.4	99.6	79.6	86.2	1.0	11.6
Diazinon	1000	75.0	95.3	79.0	83.1	1.1	10.8
Chlorpyrifos methyl	1000	72.4	94.3	76.0	80.9	1.2	11.7
Carbaryl	1000	86.4	96.5	81.3	88.1	0.8	7.7
Metolachlor	1000	78.8	98.8	80.2	85.9	1.1	11.2
Chlorpyrifos	500	76.6	98.4	79.4	84.8	2.4	11.9
Cyanazine	1000	78.3	100.6	82.9	87.3	1.2	11.8
Dacthal (DCPA)	1000	75.4	95.9	82.5	84.6	1.0	10.4
Methidathion	1000	79.3	103.1	74.4	85.6	1.5	15.4
Propargite	2000	73.6	102.1	79.8	85.2	0.7	15.0
Azinphos methyl	1000	73.3	120.4	73.7	89.1	2.7	27.1

Single day variation Day 1

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.
EPTC (Eptam)	42.8	44.5	45.5	44.3	1.4
Simazine	81.0	79.3	79.4	79.9	1.0
Diazinon	77.2	73.6	75.0	75.3	1.8
Chlorpyrifos methyl	77.9	74.0	72.4	74.8	2.8
Carbaryl	85.9	76.2	86.4	82.8	5.8
Metolachlor	82.5	82.0	78.8	81.1	2.0
Chlorpyrifos	86.7	79.2	76.6	80.8	5.2
Cyanazine	85.1	81.0	78.3	81.5	3.4
Dacthal (DCPA)	79.9	77.8	75.4	77.7	2.3
Methidathion	85.4	81.6	79.3	82.1	3.1
Propargite	79.9	85.0	73.6	79.5	5.7
Azinphos methyl	79.6	83.3	73.3	78.7	5.1

Single day variation Day 2

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.
EPTC (Eptam)	85.9	61.8	72.5	73.4	12.1
Simazine	98.0	95.5	99.6	97.7	2.1
Diazinon	104.8	96.9	95.3	99.0	5.1
Chlorpyrifos methyl	98.3	93.1	94.3	95.2	2.7
Carbaryl	104.6	91.1	96.5	97.4	6.8
Metolachlor	98.4	99.0	98.8	98.7	0.3
Chlorpyrifos	107.2	96.2	98.4	100.6	5.8
Cyanazine	103.4	101.4	100.6	101.8	1.4
Dacthal (DCPA)	98.6	96.5	95.9	97.0	1.4
Methidathion	108.0	97.0	103.1	102.7	5.5
Propargite	105.2	95.3	102.1	100.9	5.1
Azinphos methyl	118.8	104.7	120.4	114.6	8.6

Single day variation Day 3

Compound	Level 1	Level 3	Level 5	Average	Std. Dev.	
EPTC (Eptam)	80.0	36.7	68.2	61.6	22.4	
Simazine	84.6	69.1	79.6	77.8	7.9	
Diazinon	94.5	68.7	79.0	80.7	13.0	
Chlorpyrifos methyl	84.8	66.6	76.0	75.8	9.1	
Carbaryl	77.8	74.1	81.3	77.7	3.6	
Metolachlor	87.2	75.4	80.2	80.9	5.9	
Chlorpyrifos	87.3	67.6	79.4	78.1	9.9	
Cyanazine	85.9	74.0	82.9	80.9	6.2	
Dacthal (DCPA)	88.3	76.0	82.5	82.3	6.2	
Methidathion	77.2	74.9	74.4	75.5	1.5	
Propargite	65.6	74.7	79.8	73.4	7.2	
Azinphos methyl	75.2	150.7	73.7	99.9	44.0	*

Revision Log:

DATE	WHAT WAS REVISED? WHY?
1/23/05	Changed surrogate concentration to 250 ppt.
1/26/05	Added in Department SOP headers.
2/7/2005	Removed synthetic pyrethroid compounds.
4/4/2005	Changed formulas in method calibration section to reflect 500mL sample size.

Approvals:

Written By:

_____ _____
Stephen Siegel Date
Agricultural Chemist III (Supervisor)

Approved By:

_____ _____
S. Mark Lee, Ph.D. Date
Research Agricultural Chemist

Approved By:

_____ _____
Harnek Nijjar Date
Quality Assurance Officer

APPENDIX 7

ROUTINE OPERATION AND MAINTENANCE OF AGILENT/HP GC-MSD

ROUTINE OPERATION AND MAINTENANCE OF AGILENT /HP GC-MSD

1. **Purpose**:

This procedure is to be used for the start-up, shut-down, routine maintenance, and troubleshooting of Agilent (HP) GC-MSD (5971/5972/5973).

2. **Scope**:

This procedure applies to GC/MSD and shall be followed by all authorized personnel in the Center.

3. **Definitions not in Glossary**:

Detector Temperature: This term is used to refer to the transfer - line interface temperature.
EI: Electron Ionization.
EM: Electron Multiplier.
EV: Electron Volt.

4. **Outline of Procedures**:

- Instrument Start-up
- Instrument Shut-down
- Instrument Maintenance
- Instrument Troubleshooting

5. **Specific Procedures**:

5.1 Instrument Start-up

See Agilent Technologies 5973 Network Hardware Manual Chapter 2 Operating the MSD p 34
5972A MSD Manual Chapter 2, p 35
5971A MSD Manual Chapter 4, p 4 -1

5.1.1 Make sure that the computer is turned on. Turn on the GC, and make sure that all the temperatures are OFF. It is OK to allow 5-10 psi of helium to flow through the system.
5.1.2 Make sure that MSD source and its connecting cables are in perfect order and the main compartment's gasket

seal is in place and the vent-valve (5973 model) is closed. For the 5971 and 5972 MSD, make sure that the transfer-line interface unit is secured in place.

5.1.3 Make sure that a GC column has been connected to the MSD.

5.1.4 With one hand firmly holdon to the MSD unit; switch the main power to the MSD on. Release holding as soon as the vacuum seals the MSD unit in place.

5.1.5 Open up "Instrument Top" view and go to "Instrument control"

5.1.6 From the "Diagnostic and vacuum control" view, select "Pump Down".

5.1.7 Let the system pump down for 20-30 minutes before turning the oven temperature, detector temperature and injector temperature back on.

5.1.8 For the 5973 MSD, reset the MS temperatures if it has not already done so.

5.1.9 Set the oven temperature between 160-200 ° C for approximately 3-4 hr before using the MSD.

5.1.10 Instrument Pre-run system check

Mass spectrometer vacuum:

Under normal operation condition, the Ion gauge reading of the vacuum shall be 2.0 X 10^{-5} Torr or lower with the fore-pump pressure between 30-50 Torr.(See Agilent Technologies 5973 Network MSD
Hardware Manual pp. 46-47.5972A Manual, also at pp. 46-47.

5.1.10.1 Mass spectrometer air and water check

5.1.10.1.1 Set the GC oven temperature between 120 -160 °C.

5.1.10.1.2 From the "Instrument Control", go to "Diagnostics and vacuum control" view and select "Air and Water Check".

5.1.10.1.3 The abundance of ions at m/z 18 (water) and m/z 28 (nitrogen) shall be less than 10% of the abundance of 69($CF3^+$,100%, base peak fragment ions of the tuning compound, PFTBA). Or according to the of the specification method's SOP.

5.1.10.1.4 A print out report shall be used as a record.

5.1.11 Mass Spectrometer Tune and Calibration:

5973 Manual Chapter 2, p 50
5972 Manual Chapter 2, p 56
5971 Manual Chapter 4, p 4-35

5.1.11.1 Tune Compound: Perfluoro-tri-n-butyl amine [PFTBA, $(C_4F_9)_3N$],
5.1.11.2 Set the GC oven temperature at the temperature range where the expected analytes elute. In general set the GC oven temperature between 20-150 ° C. or follow the specification of the method.
5.1.11.3 Instrument Auto tune:
5.1.11.4 Go to the "Instrument Control" View
5.1.11.5 Go to Perform MS "Auto Tune" or "Manual Tune".
5.1.11.6 Select one of the following tune options
Autotune
Standard Spectra Autotune
DFTPP Tune
Maximum Sensitivity Autotune
5.1.11.7 Save the tune file and keep the print-out of the tune file for a record.

5.2 Instrument Shut-down

It is not necessary to completely shut-down the MSD after data acquisition. The system may be left in stand-by mode.

5.2.1 Instrument stand-by mode:

5.2.1.1 In general, set the GC temperature between 80-100 °C
5.2.1.2 Set GC Injector temperature between 200-230°C.
5.2.1.3 Set detector temperature at 280 °C.
5.2.1.4 Set the helium head pressure between 5-8 psi.

5.2.2 System complete shut-down

A complete shut-down of the GC-MSD is necessary for MSD service and maintenance. Also some GC service requires shut-down.

5.2.2.1 If the system is equipped with an ion gauge controller, switch off the ion gauge.
5.2.2.2 Go to the "Instrument Control" and go to "Diagnostics and Vacuum Control". Select Vent. Follow the instructions. (See also Agilent Technologies

5973 Network Hardware Manual pp. 54-56)

5.2.2.3 Shut off the oven temperature, detector temperature, and GC Injector inlet temperature .

5.2.2.4 Wait for the vent cycle to complete (approx 30-40 min.).

5.2.2.5 For the 5973 MSD, remove the top cover to expose the vent-valve.

5.2.2.6 Turn off the main power switch to the MSD and release the vacuum from the vent-valve. Disconnect the main power supply if service to the MSD is intended.

5.2.2.7 Shut off the helium flow to the GC and turn off the GC main power if necessary.

5.2.2.8 For the 5971/5972 MSD, release the vacuum by removing the GC column from the detector side.

5.3 Instrument Maintenance

See Agilent Technologies 5973 Network MSD Hardware Manual
Chapter 6 Maintaining the MSD
5972 Manual Chapter 4
5971 Manual Chapter 6

All instrument maintenance shall be recorded in the instrument's logbook.

5.3.1 Mass Spectrometer

5.3.1.1 Checking and changing fore-pump oil:
5973 Manual pp. 160 -155
5972A Manual pp. 168 - 173
5971A Manual pp. 6-14 - 6-19

5.3.1.1.1 Oil level shall be checked at least once a week.

5.3.1.1.2 Pump oil shall be changed every 4-6 months depending on usage or according to the specification of the method's SOP.

5.3.1.2 Cleaning Ion Source

(Refer to 5973 Manual pp. 206-221, pp. 230-231,
5972A Manual pp. 202 - 227;
5971A Manual pp. 6-41 - 6-58.)

5.3.1.2.1 The ion source shall be cleaned every 4-6 months depending on usage or according to the specification of the

method's SOP.

5.3.1.2.2 Follow the Agilent Technologies MSD Hardware Manual to perform ion source maintenance.

5.3.1.2.3 Replacing Electron Multiplier Replace according to the specification of the method or as needed.

5.3.2 Gas Chromatography

5.3.2.1 Replacing Inlet liner and O-ring:
Replace according to the specification of the method, or as needed

5.3.2.2 Replacing Inlet end-disk and gasket:
Replace according to the specification of the Method.

5.3.2.3 Replacing column and pre-column:
Replace according to the specification of the method

5.3.2.4 To replace and condition a GC column, follow the instructions in Agilent Technologies 5973 Network MSD Hardware Manual pp. 20 - 31.
5972A Manual, p. 18
5971A Manual, p. 4

5.3.3 Maintaining the GC/MSD Interface (5972 & 5971 MSD)
5971A Manual pp. 6-64
5972A Manual pp. 229 - 237

5.4 Instrument Troubleshooting

See Agilent Technologies 5973 Network MSD Hardware Manual Chapter 4 Troubleshooting the MSD and Chapter 5 CI Trouble shooting.
5972A MSD Manual Chapter 3, p. 63
5971A MSD Manual Chapter 5, p. A-31

6. **References**:

Agilent Technologies 5973 Network Hardware Manual
Agilent /HP 5972A MSD Hardware Manual
Agilent /HP 5971 MSD Hardware Manual

7. **Comments**:

All of the procedures described above are based on the Agilent Technologies 5973 Network Hardware Manual for instructions.

The software is revised periodically. If the steps in the Agilent Technologies 5973 Network Hardware Manual do not match your MS ChemStation software, refer to the manuals and online help supplied with the software for more information.

Reviewed By:

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Terry Jackson Date
Quality Assurance Officer

Approved By:

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William Cusick Date
Branch Chief

Revision Log:

DATE	REVISION #	REASONS FOR DEVIATION	APPROVED BY	DATE

APPENDIX 8

ROUTINE OPERATION AND MAINTENANCE OF BUCHI ROTARY EVAPORATOR

Routine Operation and Maintenance of Rotary Evaporator

1. **Purpose**:

This procedure is to be used for the basic operation, routine maintenance and troubleshooting of the rotary evaporator.

2. **Scope**:

This procedure applies to the rotary evaporator and shall be followed by all authorized personnel in the Center.

3. **Definitions not in Glossary**:

Cold finger: a round-bottomed, open top, double walled container, with a lower and upper vent for in-line vacuum condensation. The open top permits easy filling of the container with wet ice or dry ice and liquid to cool vapors rising between the walls and condense them into a receiving flask. This is a backup condensation device to prevent vaporized solvent from contaminating the vacuum pump.

Di-water: deionized or distilled water

4. **Outline of Procedures**:

- General Evaporation Considerations
- Description of Components and Operation of the Rotary Evaporator System
- Safety
- System Maintenance and Troubleshooting

5. **Specific Procedures**:

5.1 General Evaporation Considerations

5.1.1 Determine solvent's boiling point and set the water bath 10-20 °C below this point. The analytical method may specify a water bath temperature other than the range listed above. If necessary, adjust temperature of the water bath

and allow it to equilibrate. If water temperature is higher than desired, add ice to cool bath to desired temperature.
If water temperature is lower, adjust heater higher and allow to equilibrate.

5.1.2 Use Di-water exclusively in the water bath. Fill to approximately 2 cm (¾") from top of bath as a general rule when evaporating solvent from 500 mL boiling flasks.

5.1.3 Clean all sample to apparatus contacts with solvent before starting to rotary evaporate a sample.

5.1.4 Empty both condenser and cold finger collection flasks before evaporating a set of samples.

5.1.5 Check all coolant and vacuum connections for leaks or wear before starting rotary evaporation system.

5.2 Description of Components and Operation of the Rotary Evaporator System

5.2.1 The basic components consist of the following: a water bath, a vacuum pump, a cold finger and collecting flask, a chiller with a recirculating pump, a condensing column with a rotary steam vent and collecting flask for condensed solvent. A cold finger is optional.

5.2.2 Turn on chiller and allow to circulate for at least 10 minutes. Check temperature reading on front of chiller or feel tubing near condenser to make sure that the flow is cold.

5.2.3 Turn on water bath and adjust to desired temperature. Adjust water level with Di-water according to flask size.

5.2.4 Add ice to cold finger. Some sections use wet ice. If using dry ice, follow precautions listed in the Safety section 5.3.3.

5.2.5 Solvent clean the steam vent glass fitting before and after evaporating a sample. Collect the solvent washings in a waste beaker and empty into the correct waste solvent container in the hood.

5.2.6 When water bath has reached temperature attach flask to unit and clamp securely.

5.2.7 Turn on vacuum pump and adjust vacuum according to the solvent you are evaporating or the method specifications. Most solvents will evaporate well at a vacuum of 15 inches of mercury (Hg).

5.2.8 In-line vacuum selectors determine which flask/s are under a vacuum. Flow lines on the thumb holds show the direction of vacuum flow.

5.2.9 Turn rotating speed dial to begin flask rotation. If flask is quite full, begin very slowly and increase speed as solvent evaporates. If necessary, adjust water bath temperature or vacuum to control evaporation rate.

5.2.10 Lower flask into the water gradually to approximately the level of solvent in the flask. If the solvent is less than 100 mL or if it begins to boil, adjust flask height so that a rapid solvent loss is avoided.

5.2.11 Refer to the analytical method to verify the target sample volume. If specified in the method, add an exchange solvent/s and continue to evaporate until all the extraction solvent is evaporated and the approximate volume is achieved.

5.2.12 Raise flask from water bath and switch off the rotator. Vent vacuum slowly and remove flask from unit and proceed to the next step specified in the analytical method. The combi-clip may be used to remove a frozen flask from the steam vent (turn clock-wise) or to remove a jammed steam vent by moving it in the opposite directions on the threaded steam vent (Büchi pre-series R-200).

5.2.12 Depending on need, either turn off water bath and coolant pump or leave them on for the next analyst. Be sure to turn off bath and pump at the end of the day.

5.3 Safety

5.3.1 Before operation, check that all plugs and cords are in good working order and that they are plugged into the correct outlets and that they are not over loaded.

5.3.2 Check all coolant connections for leaks.

5.3.3 Use gloves to handle dry ice. Never touch dry ice with bare skin (-79 ˚C). Slowly and carefully add dry ice to cold finger.

5.3.4 Check all vacuum hose connections for a tight fit. Check for any cracking or leaks in the lines.

5.3.5 Check that the cooler-recirculator has at least 8 inches of open space around unit.

5.3.6 Check that the boiling flask has no cracks. The flask possibly implode when vacuum pressure is applied. Quantitatively transfer to a good flask with rinses, if any cracks are found.

5.4 System Maintenance and Troubleshooting

5.4.1 Check the following monthly:

5.4.1.1 Ethylene glycol level in cold finger is ~ 1/2 full
5.4.1.2 Air intakes of chiller and vacuum pump are clean and free of any obstruction
5.4.1.3 Coolant level in chiller is at the proper level
5.4.1.4 All glass joints are easy to separate and are not frozen
5.4.1.5 Water bath has no debris or sediment in it

5.4.2 Check the following yearly:

5.4.2.1 Air intakes of chiller and vacuum pump are clean and free of any obstruction
5.4.2.2 Cooling coils of the chiller are clean and free of any obstruction; if not, use a vacuum cleaner with the brush attachment to clean
5.4.2.3 Check coolant density and level. Add or change as needed

6. **References**:

None

7. **Comments**:

None

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Revision Log:

DATE	REVISION #	REASON FOR REVISION	APPROVED BY	DATE
